L14 ANSWER 1 OF 33 ZCAPLUS COPYRIGHT 1998 ACS DUPLICATE 1

AN 1996:155489 ZCAPLUS

DN 124:202047

TI Preparation of bis(dihydrodioxodibenzo[de,h]isoquinoline) derivatives and their use as anticancer agents.

IN Fernandez, Brana Miguel; Castellano, Berlanga Jose Maria; Romerdahl, Cynthia

PA Knoll Aktiengesellschaft, Germany

SO PCT Int. Appl., 20 pp.
CODEN: PIXXD2

DT Patent

LA English

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
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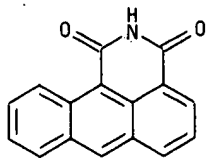
| PI | WO9529895 | A1 | 19951109 | 95WO-EP01347 | 19950412 |
| | W: AU, BG, BR, BY, CA, CN, CZ, FI, HU, JP, KR, KZ, MX, NO, NZ, PL, RU, SI, UA | | | | |
| | RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| | CA2188833 | AA | 19951109 | 95CA-2188833 | 19950412 |
| | AU9523065 | A1 | 19951129 | 95AU-0023065 | 19950412 |
| | EP-757676 | A1 | 19970212 | 95EP-0916636 | 19950412 |
| | R: CH, DE, FR, GB, IT, LI, NL | | | | |
| | CN1148851 | A | 19970430 | 95CN-0193192 | 19950412 |
| | JP09512539 | T2 | 19971216 | 95JP-0527954 | 19950412 |
| | US5703089 | A | 19971230 | 96US-0699205 | 19960819 |
| PRAI | 94US-0233998 | | 19940428 | | |
| | 94US-0332382 | | 19941031 | | |
| | 95WO-EP01347 | | 19950412 | | |

OS MARPAT 124:202047

IT ***161500-03-4P***
(prepn. of bis(dihydrodioxodibenzo[de,h]isoquinoline) derivs. and their use as anticancer agents)

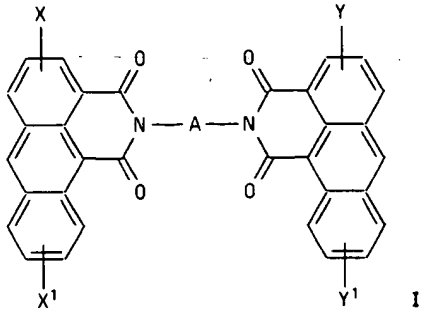
RN 161500-03-4 ZCAPLUS

CN 1*H*-Dibenz[*de*,*h*]isoquinoline-1,3(2*H*)-dione (9CI) (CA INDEX NAME)



RN 161500-03-4 ZCAPLUS

GI




I

AB Title compds. (I; X, $X^1$, Y, $Y^1$ = H, $NO_2$, $NH_2$, alkylamino, dialkylamino, acylamino, OH, alkoxy, halo, trihalomethyl, alkyl, formyl, alkylcarbonyl, ureyl, alkylureyl; A = $C_{4-12}$ bridge which is interrupted at 1-3 points by a secondary or tertiary amino group, where 2 N atoms may addnl. be bonded to one another by a $C_{1-4}$ alkylene group), were prepd. as neoplasm inhibitors (no data). Thus, anthracene-1,9-dicarboxylic anhydride was refluxed with N,N'-bis(2-aminoethyl)-1,3-propanediamine in PhMe to give 50% N,N'-bis[2-(1,2-dihydro-1,3-dioxo-3H-dibenzo[de,h]isoquinoline-2-yl)ethyl]1,3-propanediamine.

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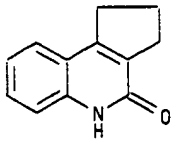
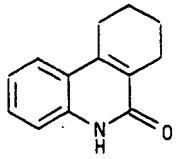
L26 ANSWER 4 OF 13 COPYRIGHT 1997 ACS
AN CA61:2985d CAOLD
IT ***4514-03-8*** ***4514-04-9***
RN 4514-03-8 CAOLD
CN 4*H*-Cyclopenta[*c*]quinolin-4-one, 1,2,3,5-tetrahydro- (7CI, 8CI, 9CI) (CA INDEX NAME)



RN 4514-04-9 CAOLD
CN 6(5*H*)-Phenanthridinone, 7,8,9,10-tetrahydro- (7CI, 8CI, 9CI) (CA INDEX NAME)



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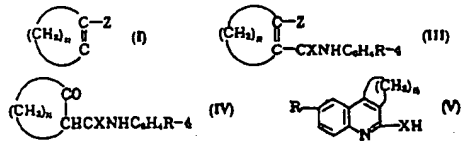
**eactions with cyclic enamines. I. Reaction of cycloalkenes with phenyl isocyanate and phenylisothiocyanate.** Walter Ried and Walter Kaeppeler (Univ. Frankfurt/Main, Ger.). *Ann.* 673, 132–6(1964). Cyclic enamines (I; Z = morpholino, *n* = 3, 4, or 5) treated with 4-$RC_6H_4NCX$ (II) (R = H or Me, X = O or S) gave β-aminocycloalkenecarboxylic and thiocarboxylic acid anilides (III), which on sapon. gave 2-oxocycloalkanecarboxylic and thiocarboxylic acid anilides (IV). IV were



cyclized with concd. $H_2SO_4$ to V. Enamines were prepd. according to Huenig, *et al.* (*CA* 52, 15443*a*). I (*n* = 5) $b_{12}$ 138°. I (0.1 mole) in 50 cc. $CHCl_3$ added dropwise with stirring to 0.1 mole II (R = H, X = O) or 0.1 mole II (R = H, X = S) in 50 cc. $CHCl_3$, the soln. let stand a few min. and refluxed 5 min., the $CHCl_3$ removed *in vacuo* quant. as far as possible, the residual oil cooled (in some cases sprayed with MeOH), and the solid recrystd. from MeOH gave the following III (X, *n*, R, m.p., and % yield given): O, 3, H, 127°, 92; O, 4, H, 132°, 93; O, 5, H, 130°, 92; S, 3, H, 122°, 93; S, 4, H, 127°, 93; S, 5, H, 119°, 83; S, 4, Me, 121–2°, 78 [in this case 0.1 mole I (*n* = 5) and 0.1 mole II (R = Me, X = S) was heated 15 min. without any solvent and worked up]. III (3 g.) dissolved in 30 cc. 70% $H_2SO_4$ and kept overnight at 0°, the soln. poured on 100 g. ice, and the ppt. filtered off gave the following IV, adequately pure for cyclization [X, *n*, R, m.p. (cyclohexane), and % yield given]: O, 3, H, 104°, 73; O, 4, H, 106°, 75; O, 5, H, 101°, 71; S, 3, H, 94°, 70; S, 4, H, 97°, 86; S, 5, H, 93.5°, 73; S, 4, Me, 92.5°, 70. Crude IV (~1 g.) and 3 cc. concd. $H_2SO_4$ heated 15 min. at 100°, the soln. poured on 50 g. ice, and the ppt. filtered off, washed with cold EtOH, and recrystd. from $HCONMe_2$ gave the following V (X, *n*, R, m.p., and % yield given): O, 3, H, 158°, 67; O, 4, H, 273°, 73; O, 5, H, 270°, 70; S, 3, H, 246° (decompn.), 71; S, 4, H, [illegible]° (decompn.), 76; S, 5, H, 239–40° (decompn.), 68; S, 4, 262° (decompn.), 69.

William Braker

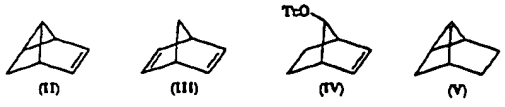
**echnological problems of the synthesis of bicyclo[2.2.1]-2,5-heptadiene. I.** Jan Orlowski, Piotr Swiatkowski, and Marek Cieslak (Inst. Org. Ind., Warsaw). *Przemysl Chem.* 43(4), 210–13(1964). Calcns. based on thermodynamic data have been used to show that the equil. and the rate of monomerization of cyclopentadiene dimer are favorable for its use with acetylene to synthesize bicyclo[2.2.1]-2,5-heptadiene at temps. up to 400°.

Eugene A. Lojewski

**Catalytic conversions of spiro[5.6]dodecane on a platinum catalyst.** N. V. Elagina, A. K. Mirzaeva, Kh. E. Sterin, A. V. Bobrov, and B. A. Kazanskii. *Neftekhimiya* 4(2), 241–5(1964); cf. *CA* 60, 1617*c*. Spiro[5.6]dodecane (I) (29.2 g.) was passed without carrier gas over 15% Pt on C at 320° at a space velocity of 0.2 $hr.^{-1}$ The gaseous products amounted to 13 l. and consisted of 94.7% H and 5.3% $CH_4$. The liquid product was analyzed by fractional crystallization and gas chromatography, and consisted of 40 wt. % $Pb_3$, 34% unreacted I, 11% *n*-hexylbenzene, 6% 1,2-benzobicyclo[0.3.3]octane, 4% benzocycloheptane, 1% dicyclohexyl, and 1% *n*-pentylbenzene. The products were accounted for by a mechanism involving rupture at the quaternary C, followed by a series of isomerization and aromatization reactions.

K. L. Olivier

**Reaction of 7-norbornadienyl and 7-dehydronorbornyl derivatives with borohydride under solvolytic conditions—evidence for the tricyclic nature of the corresponding cations.** Herbert C. Brown and Harold M. Bell (Purdue Univ., Lafayette, Indiana). *J. Am. Chem. Soc.* 85(15), 2324(1963). The reaction of 7-chloronorbornadiene (I) in 65% aq. diglyme 1.8*M* in $NaBH_4$ afforded 83% II and 12% III. Under the same conditions, IV



gave 15% of V, 70% norbornene (VI), and 6–7% *anti*-dehydronorborneol. With $LiAlH_4$ in tetrahydrofuran IV reacted rapidly to give 60% V and 34% VI. Solvolysis of I and IV under weakly alk. conditions in the absence of $NaBH_4$ gave, resp., 7-norborn[illegible]nol and *anti*-7-norborneol. The high yields of tricyclic hy[illegible]rbons appear to be more easily rationalized in terms of [illegible]ibrated classical carbonium ions rather than nonclassical carbonium ions.

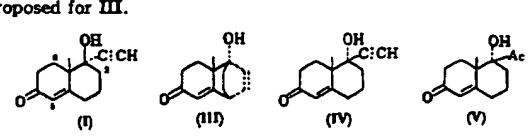
T. W. Brooks

**2,4-Dimethyltricyclo[1.1.1.$0^{2,4}$]pentan-5-one.** W. v. E. Doering and Martin Pomerantz (Yale Univ.). *Tetrahedron Letters* 1964(17–18), 961–6. Irradiation of a soln. of Me diazoacetate and 2-butyne gave Me 1,2-dimethylcyclopropene-3-carboxylate (I). I upon sapon. with KOH in refluxing MeOH gave 1,2-dimethylcyclopropene-3-carboxylic acid (II), m. 77–8° (pentane). Reesterification of II gave pure I. Treatment of II with oxalyl chloride gave the acid chloride, which with MeOH regenerated I and with $NH_3$ gave 1,2-dimethylcyclopropene-3-carboxamide, m. 152–3°. I reacted with butadiene 43 hrs. at 78° to give Me *cis*-1,6-dimethylbicyclo[4.1.0]hept-3-ene-7(*endo*)-carboxylate; free acid m. 168.5–9.0°. The acid chloride with 2 equivs. $CH_2N_2$ gave the diazoketone (III); III refluxed in hexane with Cu powder gave 2,4-dimethyltricyclo[1.1.1.$0^{2,4}$]pentan-5-one (IV), m. 57–8°, in about 1% yield. Catalytic hydrogenation of IV pro-

ceeded slowly over Pt in MeOAc with absorption of 2 moles of H in 12 hrs. to give 45% and 27%, resp., *cis*- and *trans*-3,4-dimethylcyclopentanone in addn. to 28% unchanged IV. The structure of IV was supported by mass. infrared, and nuclear magnetic resonance spectra. IV failed to react with semicarbazide-HCl, reacted readily with iodine, and when heated 20 hrs. at 156° in the presence of hydroquinone gave only polymeric material. IV heated 24 hrs. at 198° with di-Me acetylenedicarboxylate gave dimethyl 4,5-dimethylphthalate and another product.

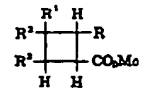
B. K. Wasson

**An unusual 1,4-bridging in a cyclohexane ring via an acetylenic function.** S. Swaminathan, S. Ramachandran, and S. K. Sankarappa (Univ. Madras, India). *Tetrahedron* 20(5), 1119–23 (1964). I, m. 172–3° (Nazarov and Gurvich, *CA* 50, 5600*e*) (10 g.), in 75 ml. MeOH was stirred 6 hrs. at 60° with Nieuwland's catalyst (II) (Hennion, *et al.*, *CA* 28, 4374[1]), prepd. from 1.3 g. HgO, 1.5 ml. $BF_3$ etherate, and 1.5 ml. MeOH, the mixt. treated with 10 g. $K_2CO_3$, the filtered soln. concd. and extd. with $CHCl_3$ and the dried ext. evapd. to give 6 g. 1β-hydroxy-6-oxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydro-1α,4α-ethenonaphthalene (III); Ac deriv., prepd. with $Ac_2O$-*p*-$MeC_6H_4SO_3H$, m. 122–3°; $BrCH_2CO$ deriv. m. 132–3°. When the HgO was omitted and the reaction product was chromatographed, 70% of a mixt. of I and its epimer (IV) was obtained. IV treated with II in the same way as I gave about 30% 1α-hydroxy-1β-acetyl-6-oxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene (V), m. 133–3.5°. Redn. of 2 g. III with Li in $NH_3$ gave 1.2 g. of a dihydro compd., $C_{13}H_{18}O_2$, m. 68–9°. 2-Methyl-1,3-cyclohexanedione (12.6 g.) when refluxed 3 hrs. with MeI and 0.4 g. K in 50 ml. MeOH gave 82% 2,2-dimethyl-1,3-cyclohexanedione, $b_{11}$ 103–5°, m. 39–40°, which (31.8 g.) treated with HC:CLi (from 1.6 g. Li) in 200 ml. $Et_2O$ with the addn. of HC:CH gave 26 g. 1-ethynyl-1-hydroxy-2,2-dimethyl-3-oxocyclohexane (VI), m. 91–1.5°. VI treated with II gave 1-acetyl-1-hydroxy-2,2-dimethyl-3-oxocyclohexane, m. 124–5°. On the basis of nuclear magnetic resonance and infrared spectra the given structural formula is proposed for III.



F. E. Brauns

**Amino-substituted cyclobutanecarboxamides.** Armin G. Wilson and Leonard Weintraub (to Bristol-Myers Co.). U.S. 3,133,924 (Cl. 260–268), May 19, 1964, Appl. May 31, 1960; 9 pp. The title compds. are used as analgesics with longer analgesic effect than other cyclobutane derivs., as central nervous system depressants as sludge and color stabilizers in fuel oil, and, in combination with phenolic materials, as antioxidants in gasoline. A mixt. of 139 g. *N*-isobutenylpiperidine and 86 g. $CH_3$:$CHCO_2Me$ was autoclaved 2 hrs. at 180° to give 70% I (R = 1-piperidyl, $R^1$ = $R^2$ = Me, $R^3$ = H), $b_{0.7}$ 103°, $n^{25}D$ 1.4705. Similarly were prepd. the following I:



| R | $R^1$ | $R^2$ | $R^3$ | b.p./mm. | $n^{25}D$ |
|---|---|---|---|---|---|
| $NMe_2$ | Me | Me | H | 49–50°/1.5 | 1.4448 |
| morpholino | Me | Me | H | 101–2°/2.2 | 1.4711 |
| $NBu_2$ | Me | Me | H | 98°/1.5 | 1.4563 |
| iso-$Bu_2N$ | Me | Me | H | 93–100°/2 | 1.4510 |
| $CO_2Me$ | Me | $NMe_2$ | H | 93–4°/1.5 | 1.4502 |
| $CO_2Et$ | Me | Me | piperidino | 113–20°/1.0–1.5 | 1.4663 |
| piperidino | Et | Et | H | 119–21°/2 | 1.4788 |

1,4-Bis(4-methoxycarbonyl-2,2-dimethylcyclobutyl)piperazine m. 148°. $Me_2CHCHO$ (180 g.) was added to $Bu_2NH$ over 1/3 hr. and the mixt. refluxed 12 hrs. (30 ml. $H_2O$ collected) to give 63% $Me_2CH$:$CHNR_2$ (R = Bu) (II), $b_{4.4-4.7}$ 70–2°, $n^{25}D$ 1.4409.

L5 ANSWER 5 OF 8 BEILSTEIN COPYRIGHT 1998 BEILSTEIN CD&S
Justus Liebigs Ann. Chem., 388 <1912>, 212, CODEN: JLACBF
Note(s):
3. Handbook Data
PRE
Start: BRN=2869591 anthraquinone-carboxylic acid-(1)-ethyl ester
Reag: pyridine, hydrazine hydrate
Reference(s):
1. Ullmann; van der Schalk, Justus Liebigs Ann. Chem., 388 <1912>, 212, CODEN: JLACBF
Note(s):
2. Handbook Data
PRE
Reference(s):
1. Dokunichin; Fain, J.Gen.Chem.USSR (Engl.Transl.), 34 <1964>, 2385, CODEN: JGCHA4
Zh.Obshch.Khim., 34 <1964>, 2372, CODEN: ZOKHA4
2. Gomes, C.R.Hebd.Seances Acad.Sci.Ser.C, 272 <1971>, 668, CODEN: CHDCAQ
3. Dokunichin; Fain, J.Gen.Chem.USSR (Engl.Transl.), 34 <1964>, 3819, CODEN: JGCHA4
Zh.Obshch.Khim., 34 <1964>, 3769,3819, CODEN: ZOKHA4

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L20 ANSWER 1 OF 3 ZCAPLUS COPYRIGHT 1997 ACS
AN 1967:463893 ZCAPLUS
DN 67:63893
TI Aryl amides of 2-arylamino-1-cyclopentene-1-carbo-thionic acids and their use in the synthesis of heterocyclic compounds
AU Schoen, Jadwiga; Bogdanowicz-Szwed, Krystyna
CS Univ. Cracow, Cracow, Poland
SO Rocz. Chem. (1967), 41(1), 89-101
CODEN: ROCHAC
DT Journal
LA Polish
GI For diagram(s), see printed CA Issue.
AB Addn. of cyclopentanone anils to ArNCS (Ar = Ph, p-MeC6H4, or p-ClC6H4) led to arylamides (Ia, Y = NHR) (I) of 2-arylamino-1-cyclopentene-1-carbothionic acids which were transformed to 1,3-diaryl-2-oxo-4-thioxo-5,6-cyclopenteno-1,2,3,4-tetrahydropyrimidines (II) by condensation with COCl2. Hydrolysis of I led to the aryl amides (Ia, Y = OH) (III) of 2-hydroxy-1-cyclopentene-1-carbothionic acid, which were cyclized to 2-mercapto-3,4-cyclopentenoquinolines (IV) (R = SH). A soln. of 17 g. cyclopentanone and 25 g. PhNH2 in 200 ml. C6H6 was refluxed 2 hrs. with 0.5 g. aniline zinc chloride until 3.6 ml. H2O was removed, and distd. to give 15.5 g. 1-(NHR substituted)-1-cyclopentene V (R = Ph), b15 125-30.degree.. Heating 17 g. cyclopentanone with 25 g. p-MeC6H4NH2 during 30 min. to 100.degree., then treatment with small portions of 0.5 g. p-toluidine zinc chloride and heating 1 hr. to 150.degree. afforded 12 g. V (R = p-MeC6H4), b8 130-5.degree.. Similarly prepd. was V (R = p-ClC6H4), b6 135-8.degree.. An equimolar mixt. of 0.05 mole V and ArNCS was heated 2 hrs. at 120.degree., and dild. either with 25 ml. EtOH or a mixt. of C6H6-EtOH (1:1) to give a cryst. product, which was sepd. from the diarylthiourea by crystn. from C6H6. The following I were reported (R, R1, m.p., and % yield given): Ph, Ph (VI), 129-31.degree., 74; Ph, p-MeC6H4, 142-3.degree., 31; Ph, p-ClC6H4, 148-9.degree., 46; p-MeC6H4, Ph, 115-16.degree., 56; p-MeC6H4, p-MeC6H4, 155-6.degree., 20; p-MeC6H4, p-ClC6H4, 147-9.degree., 55; p-ClC6H4, Ph, 143-5.degree., 58; p-ClC6H4, p-ClC6H4, 163-4.degree., 50. A hot soln. of 0.005 mole I in 25 ml. PhMe was treated dropwise at 50-80.degree., during 40 min. with 5 ml. 20% COCl2 in PhMe, the mixt. left overnight, decanted, and the oily residue triturated with 20 ml. ligroine to give II. The following II were prepd. (R, R1, m.p., and % yield given): Ph, Ph, 145-7.degree., 61; Ph, p-MeC6H4, 129-31.degree., 49; Ph, p-ClC6H4, 128-30.degree., 21; p-MeC6H4, p-MeC6H4, 209-10.degree., 70; p-MeC6H4, p-ClC6H4, 137-9.degree., 55; p-ClC6H4, Ph, 170-1.degree., 38; p-ClC6H4, p-ClC6H4, 176-8.degree., 47. Hydrolysis of 1 g. VI in 50 ml. EtOH with 10 ml. 6% HCl during 30 min. under reflux, followed by distn. of 25 ml. EtOH and diln. with 250 ml. H2O led to 0.6 g. III (R 1 = Ph), m. 94-6.degree.. Similarly prepd. were the following III (R1 and m.p. given): p-ClC6H4, 104-6.degree.; p-MeC6H4, -. A mixt. of 2 g. IV (R = OH, X = H) (VII), 3 g. PCl5, and

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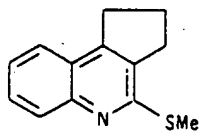
30 ml. POCl3 was refluxed 30 min., distd. to remove 20 ml. POCl3, and the residue poured into 100 ml. H2O to give 1.3 g. IV (R = Cl, X = H) (VIII), m. 118-20.degree. (MeOH). Cyclization of 1.5 g. III (R1 = Ph) in 15 g. concd. H2SO4 (method A) during 30 min. on a steam bath followed by pouring into 200 g. ice water led to 12 g. IV (R = SH, X = H) (IX), m. 293-4.degree. (AcOH). IX was also prepd. from 4 g. VII and 14 g. P2S5 when refluxed 5 hrs. in 150 ml. PhMe. The ppt. formed extd. with hot AcOH gave after concn. and diln. with water 1 g. IX. Similarly, a boiling soln. of 13 g. S:C(NH2)2 in 100 ml. EtOH treated portionwise with 3 g. VIII (method B), then refluxed 15 min., cooled, and neutralized with Na2CO3 afforded 3 g. IX; Me thio ether m. 81-3.degree.; PhCH2 thioether m. 89-91.degree.; SCH2CO2H analog m. 160-2.degree.. Similarly prepd. were the following IV (R, X, m.p., and method given): SH, Cl, 290-2.degree., A and B; SH, Me, 272-4.degree., A. A distg. soln. of 15 g. carbethoxy-2-cyclopentanone in 25 ml. xylene was treated dropwise, during 1 hr., with a mixt. of 12 g. p-ClC6H4NH2, 25 ml. xylene, and 1 ml. pyridine. After 50 ml. distillate had been collected, the residue was cooled and dild. with 25 ml. ligroine to give 25 g. p-chloroanilide of 2-hydroxy-1-cyclopentene-1-carboxylic acid (X), m. 115-17.degree. (C6H6-ligroine, 1:4). A cold soln. of 13 g. X in 130 g. concd. H2SO4 heated 15 min. on a water bath and poured into ice afforded 7 g. IV (R = OH, X = Cl) (XI), m. 291-2.degree. (AcOH). When refluxed 30 min. and worked up as above a mixt. of 2 g. XI, 3 g. PCl5, and 30 ml. POCl3 gave 1.3 g. IV (R = X = Cl), m. 184-6.degree. (AcOEt). V (R = Ph) (9 g.) treated dropwise during 45 min. at 20.degree. with 7 g. PhNCO, and the mixt. heated 1.5 hrs. at 120.degree., and dild. with 20 ml. C6H6 afforded 7.7 g. 2-anilino-1-cyclopentene-1-carboxylic acid anilide (XII), m. 128-30.degree. (MeOH). XII was also prepd. from the above substrates using benzene as the solvent.

IT ***15882-30-1P***

(prepn. of)

RN 15882-30-1 ZCAPLUS

CN 1*H*-Cyclopenta[*c*]quinoline, 2,3-dihydro-4-(methylthio)- (8CI) (CA INDEX NAME)

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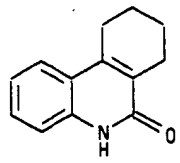
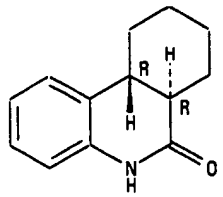
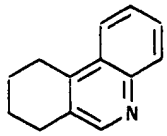
L26 ANSWER 5 OF 13 COPYRIGHT 1997 ACS
AN CA60:11984b CAOLD
IT ***4514-04-9*** ***39161-10-9*** ***62833-92-5***
RN 4514-04-9 CAOLD
CN 6(5*H*)-Phenanthridinone, 7,8,9,10-tetrahydro- (7CI, 8CI, 9CI) (CA INDEX NAME)



RN 39161-10-9 CAOLD
CN 6(5*H*)-Phenanthridinone, 6a,7,8,9,10,10a-hexahydro-, *trans*- (9CI) (CA INDEX NAME)
Relative stereochemistry.



RN 62833-92-5 CAOLD
CN Phenanthridine, 7,8,9,10-tetrahydro- (6CI, 7CI, 9CI) (CA INDEX NAME)



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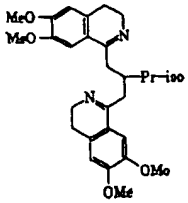
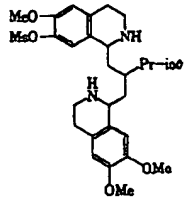
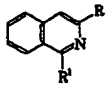
(XXXIV), m. 182°, and a little XXXV, m. 222–3° (EtOH). Hydrolysis of XXXIV with aq. HCl gave 90% iso-PrCH($CH_2CO_2H$)$_2$ (XXXVI), m. 102° ($H_2O$); 72% di-Me ester (XXXVII) $b_{12}$ 124–6°. VIII (18.1 g.) and 9 g. XXXVI heated 4 hrs. at 190° (bath) gave 12 g. mixt. of *N*-homoveratryl-3-isopropylglutarimide (XXXVIII) and iso-PrCH[$CH_2CONHCH_2CH_2C_6H_3$(OMe)$_2$-3,4]$_2$ (XXXIX), m. 131–1.5°; after several days the filtrate deposited 2.6 g. XXXIX, m. 156° (EtOH); from this mother liquor was isolated 1 g. XXXIX, m. 155–6° ($Me_2CO$). VIII (9.05 g.) and 5.05 g. XXXVII heated 3 hrs. at 190° (bath) in an open vessel gave 8–10 g. XXXIX, m. 156–7°; from the filtrate was isolated 2.5–3.0 g. XXXVIII, m. 119.5–20° (EtOH). The mixt. (m. 131.5°) (1.69 g.) of XXXVIII and XXXIX refluxed 12 hrs. in 50 cc. 2*N* NaOH gave 0.25 g. XXXIX, m. 156°; the filtrate made just acid to Congo red with 18% HCl and extd. with 1:1 $Et_2O$–$C_6H_6$ gave 0.05 g. 3,4-$(MeO)_2C_6H_3CH_2CH_2NH$-$COCH_2CH$(Pr-iso)$CH_2CO_2H$, m. 129° (MeCO). XXXIV (4.7 g.), 15 cc. $POCl_3$, and 50 cc. anhyd. PhMe refluxed 4 hrs. gave 1.05 g. mixt. of XXXVIII and XXXIX, m. 131°, and 0.35 g. XL; and dipicrate m. 195–6° (EtOH). When 25 g. $P_2O_5$ was used instead of $POCl_3$, 2.2 g. XL was obtained. XL (2.2 g.) in 25 cc. MeOH

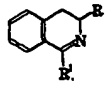

(XLI)


(XLI

reduced with 0.5 g. $NaBH_4$ in 10 cc. $H_2O$ gave 1.87 g. XLI; di-HCl salt m. 228–30° (anhyd. iso-PrOH). XXIV and XLI.2HCl were much less active than emetine-HCl as amebicides. The infrared spectra of the mixt. of XXXVIII and XXXIX and of XXXIX were recorded. Martin J. Braker

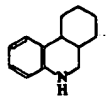
Isoquinoline derivatives. XV. Cyclization of ethyl α-aryl(or alkaryl)-α-acylamido-β-phenylpropionate. Bhabatosh Bhattacharya (Bengal Immunity Res. Inst., Calcutta). *Indian J. Chem.* 2(1), 25–7(1964); cf. *CA* 55, 23538*a*; 60, 2888*a*. 5-Benzyl-5-phenylhydantoin (250 g.) was refluxed 30 hrs. with 3 l. 45% aq. KOH, the mixt. filtered, the filtrate acidified (Congo) with HCl, filtered again, evapd. to dryness, extd. with abs. EtOH, and the ext. concd. and neutralized (pH 6) with $C_5H_5N$ to give 90 g. $PhCH_2CPh(NH_2)CO_2H$ (I), m. 279–80° (decompn.) (aq. EtOH); Ac deriv. m. 284–5° (decompn.) (EtOH). An ethanolic soln. of I on satn. with dry HCl at 3–4° 60–70 hrs. gave the Et ester (II), $b_{4-6}$ 176–8°, $n_D^{25}$ 1.5585; picrate m. 202–3° (EtOH). Similarly, hydrolysis of 5,5-dibenzylhydantoin with 50% aq. NaOH gave $PhCH_2CBz(NH_2)CO_2H$ (III), m. 307–8° (decompn.); Ac deriv. m. 250–1° (decompn.) (EtOH). III Et ester (IV) m. 66–9° (aq. EtOH); picrate m. 195–6° (EtOH). Treatment of 0.1 mole II or IV with 0.12 mole of the appropriate acid chloride in the presence of 60 ml. 10% aq. NaOH gave Et α-aryl(or alkaryl)-α-acylamido-α-phenylpropionates (V). The following V were prepd. (aryl or alkaryl group, acylamido group, % yield, and m.p. given): Ph, NHAc (VI), 59.3, 92–3°; Ph, NHBz, 91, 87–8°; Ph, $NHCOCH_2Ph$, 80, 108–7°; Bz, NHAc, 60.3, 126–7°; Bz, NHBz, 93.5, 109–10°; and Bz, $NHCOCH_2$-Ph, 93.5, 113–14° (all compds. were crystd. from EtOH except VI from petr. ether). V (1 part) and 4 parts $P_2O_5$ was refluxed 6 hrs. in 20 parts xylene (dry atm.), the evolved CO collected, and the mixt. worked up to give isoquinolines. The following


(VII)


(VIII)

VII were prepd. [R, R¹, % yield, CO obtained (as % of the theoretical), m.p. or b.p., $n_D^{25}$, m.p. HCl salt, and m.p. picrate given]: Ph, Me, 38.7, 52.7, 48–9°, —, 211–12°, 204–5°; Ph, Ph, 31.3, 67.02, 78–9°, —, 123–8°, 168–9°; Ph, Bz, 34.5, 71.0, 71–2°, —, 249–50°, 188–9° (decompn.); Bz, Me, 56, 56.90, $b_{2-3}$ 179–80°, 1.5998, —, 175–6°; Bz, Ph, 16.4, 59.50, $b_{2-3}$ 210–12°, 1.6504, —, 175–6°; and Bz, Bz, 16.2, 62.00, $b_{1-3}$ 202–4°, 1.6256, —, 166–7°. The structures of VII were confirmed by the superimposable ultraviolet spectra of VII with those obtained by dehydrogenation of the corresponding 3,4-dihydro isoquinolines (VIII). The yield of VIII was improved by the use of $P_2O_5$ as condensing agent in place of $POCl_3$. Thus, 1 part α-acyl-α-benzylphenethylamide, 3 parts $P_2O_5$, and 10 parts PhMe was refluxed 5–6 hrs., cooled, treated with ice-water to decompose $P_2O_5$, and the clear soln. basified with aq. NaOH to give the resp. VIII. VIII were dehydrogenated at 240–5° with Tetralin and 10% Pd–C in a $CO_2$ atm. to yield VII. The following VIII (R = Bz) were prepd. (R¹, % yield, b.p., m.p. picrate, and b.p. of dehydrogenated product given): Me, 70, $b_{2-4}$ 174–5°, 148–9°, $b_{2-3}$ 179–80°; Ph, 55, $b_{4-5}$ 228–30°, 172–3°, $b_{2-3}$ 210–12°; and Bz, 42, $b_{2-4}$ 224–5°, 171–2°, $b_{1-3}$ 202–4°. The present findings supported earlier observations (Ghosh and B., *loc. cit.*) and pointed to the general applicability of the reaction. V. K. Ahluwalia

Condensed polynuclear perhydro compounds containing nitrogen. XII. Synthesis and exhaustive methylation of 5,6,6a,7,8,9,10,10a-octahydrophenanthridines and related compounds. Tadashi Masamune, Mitsuo Takasugi, Hiroshi Suginome, and Masayo Yokoyama (Hokkaido Univ., Sapporo, Japan). *J. Org. Chem.* 29(3), 681–5(1964); cf. *CA* 53, 5234*d*; 54, 14251*d*. Several methods for the prepn. of *trans*- and *cis*-5,6,6a,7,8,9,10,10a-octahydrophenanthridines (*cis*-I) were described. Confirmation of the configuration of I by stereospecific synthesis and the conformation of *cis*-I were discussed. Ex-


(I)

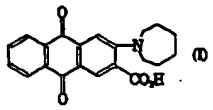
haustive methylation of the stereoisomeric I and octahydroacridines resulted in elimination of MeOH. VNJZ

Synthesis of *N*-(5-dimethylaminoamyl)-3-azabicyclo[3.3.1]-nonane. Silvano Rossi and Carmela Valvo (Lab. Farm. Maestretti S.p.A., Milan). *Chim. Ind.* (Milan) 42(6), 637–8(1960). The title compd. (I) was prepd. for its potential ganglioplegic


(I)

activity. A mixt. of 11.3 g. glutarimide in 45 cc. alc. and 6 g. $Me_2NH$ warmed in a sealed tube 7 hrs. at 100–10°, concd., triturated with $Et_2O$ and recrystd. from EtOAc gave *N,N*-dimethylglutaramide (II), m. 97–8°. II (6 g.) in 80 cc. tetrahydrofuran was added to 3.6 g. $LiAlH_4$ in tetrahydrofuran, and the mixt. refluxed 3 hrs. and decompd. with 0.6 g. NaOH in 18 cc. $H_2O$ to give *N,N*-dimethylcadaverine, $b_3$ 54°. Heating this with hexahydroisophthalic anhydride 16 hrs. at 140° gave *N*-(5-dimethylaminoamyl)hexahydroisophthalimide, $b_{0.05}$ 197–8°; picrate m. 112–14° (alc.). Redn. of this in $Et_2O$ with $LiAlH_4$ gave I, $b_1$ 116–18°; picrate m. 164–6° (alc.). Treatment with MeI in $Me_2CO$ at room temp. gave the terminal quaternary salt, m. 172–4° (alc.-$Et_2O$). L. M. Werbel

Halogen substitution in chloro- and nitrochlorocarboxylic acids. V. N. Lisitsyn. *Tr. Vses. Mezhvus. Nauchn.-Tekhn. Konf. po Vopr. Sintesa i Primenenija Organ. Krasitelei, Ivanovo* 1961, 51–6(Pub. 1962). Heating *o*-chlorobenzoic acid, 3′-chloro-2,4′-benzophenonedicarboxylic acid, or 2-chloro-3-anthracenecarboxylic acid with 11–13% aq. hexamethylenimine [side product from production of $NH_2(CH_2)_6NH_2$ in the presence of $CuCl_2$ and metallic Cu in an autoclave at 150–60° resulted in formation of 70% *o*-hydroxybenzoic acid, 71% 3′-hydroxy-2,4′-benzophenonedicarboxylic acid, and 54% 2-hydroxy-3-anthracenecarboxylic acid, resp. It was hypothesized that the substitution of the Cl atom at the *o*-position with respect to the carboxyl group with a hydroxy group takes place through a Cu salt and a hexatomic chelate ring. The presence of 1 or 2 nitro groups at the *o*- and (or) *p*-position with respect to the Cl atom aided substitution of the latter (under the same conditions) by a hexamethylenimino group. The Cl atom in anthraquinone and 3-anthraquinonecarboxylic acid is easily replaced by a hexamethylenimino group in the absence of Cu


(II)

or Cu salts, resulting in formation of 95% 2-hexamethyleniminoanthraquinone, m. 150.5–1.5°, and 94% 2-hexamethylenimino-3-anthraquinonecarboxylic acid (I), m. 191.0–2.0°. The following were also obtained (% yield and m.p. given): 3-nitro-4-hexamethyleniminobenzoic acid, 83, 189.0–9.5°; 5-nitro-2-hexamethyleniminobenzoic acid, 70–3, 168.5–9.3°; 3,5-dinitro-2-hexamethyleniminobenzoic acid, 93, 125.0–6.0°; 3,5-dinitro-2-hexamethyleniminobenzoic acid, 91, 216.5–17.5°. From *Ref. Zh., Khim.* 1963, Abstr. No. 13Zh144. MVRK

Epoxy alkyl esters. Shell Internationale Research Maatschappij N.V. Brit. 936,803 (Cl. C 07*d*), Sept. 11, 1963; Neth. Appl. May 19, June 30, and Nov. 30, 1959; 10 pp. Epoxyalkyl- or epoxycycloalkyl esters of an α-alkylalkanemonocarboxylic acid (I) are discussed in the invention. The ester may be prepd. from the reaction of the salt of an acid and an epoxyalkyl halide or a halohydrin. Thus, 1 mole of the dry

L14 ANSWER 2 OF 33 ZCAPLUS COPYRIGHT 1998 ACS

AN 1995:546011 ZCAPLUS

DN 122:316902

TI Design and synthesis of near-infrared absorbing pigments. II. Structure determination of aceanthrene green and derivatives

AU Deselets, Denis; Kazmaier, Peter M.; Burt, Richard A.; Hamer, Gordon K.

CS Xerox Res. Cent. Canada, Mississauga, ON, L5K 2L1, Can.

SO Can. J. Chem. (1995), 73(3), 325-35
CODEN: CJCHAG; ISSN: 0008-4042

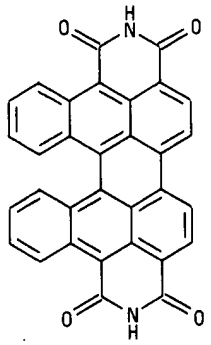
DT Journal

LA English

IT ***6424-79-9***
(contaminant; prepn. and structure detn. of aceanthrene green and derivs.)

RN 6424-79-9 ZCAPLUS

CN Dibenzo[*h*,*h'*]phenanthro[2,1,10-*def*:7,8,9-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetrone (9CI) (CA INDEX NAME)

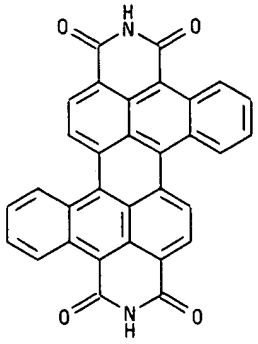


IT ***163685-87-8P***
(prepn. and structure detn. of aceanthrene green and derivs.)

RN 163685-87-8 ZCAPLUS

CN Dibenz[*h*,*h'*]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetrone (9CI) (CA INDEX NAME)

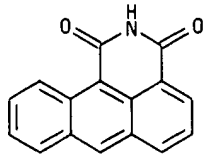
RN 163685-87-8 ZCAPLUS



IT ***161500-03-4*** , 1,9-Anthracenedicarboxylic imide
(starting material; prepn. and structure detn. of aceanthrene green and derivs.)

RN 161500-03-4 ZCAPLUS

CN 1*H*-Dibenz[*de*,*h*]isoquinoline-1,3(2*H*)-dione (9CI) (CA INDEX NAME)



AB The reported structure of aceanthrene green, a pigment prepd. by KOH fusion of 1,9-anthracenedicarboximide, was found to be incorrect. The structure of the pigment was reassigned to 7,8,15,16-dibenzo[a,j]perylenetetracarboxylic diimide on the basis of COSY, NOESY, and inversion-recovery $^1$H NMR expts. N-alkyl- or N-phenyl-1,9-anthracenedicarboximides, aceanthryleno[1,2-b]quinoxaline, and a benzimidazole deriv. of 1,9-anthracenedicarboxylic anhydride were found to give the same dibenzo[a,j]perylene structure when reacted in KOH. The electronic spectra of these derivs. were reported and, as predicted by PPP calcns. they absorbed in the near-IR. A mechanistic outline for the fusion was proposed on the basis of AM1 and frontier MO calcns.

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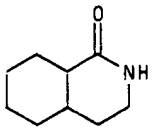
L18 ANSWER 6 OF 19 COPYRIGHT 1997 ACS
AN CA61:16004h CAOLD
IT ***20597-65-3***
RN 20597-65-3 CAOLD
CN Isocarbostyril, octahydro- (6CI, 7CI, 8CI) (CA INDEX NAME)



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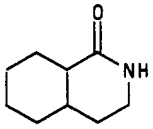
L18 ANSWER 7 OF 19 COPYRIGHT 1997 ACS
AN CA61:11967h CAOLD
IT ***20597-65-3***
RN 20597-65-3 CAOLD
CN Isocarbostyril, octahydro- (6CI, 7CI, 8CI) (CA INDEX NAME)



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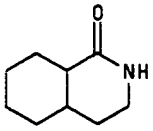
L18 ANSWER 8 OF 19 COPYRIGHT 1997 ACS
AN CA60:6821b CAOLD
IT ***20597-65-3***
RN 20597-65-3 CAOLD
CN Isocarbostyril, octahydro- (6CI, 7CI, 8CI) (CA INDEX NAME)



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position: *p*-$HO_3SC_6H_4N$:N (I), $Cu^{++}$, 6.9 × $10^{-14}$; *o*-$HO_3CC_6H_4N$:N (II), $Cu^{++}$, 6.3 × $10^{-12}$. For $Ni^{++}$ 4 × $10^{-13}$ and 6.4 × $10^{-11}$, resp., and for $Co^{++}$, 3.78 × $10^{-13}$ and 1.4 × $10^{-12}$, resp. These complexes evidently contain the metal in chelate form between the 1- and the 8-positions. In acid soln. the following values of equil. constants were detd. in respect to $H^+$ ions: I, pH 4, Cu, 5 × $10^{-6}$; pH 5, $Ni^{++}$, 7 × $10^{-6}$; pH 5, $Co^{++}$, 1.15 × $10^{-6}$; II, pH 3.5, $Cu^{++}$ 1.28 × $10^{-6}$; pH 5, $Ni^{++}$ 6.4 × $10^{-6}$; pH 5, $Co^{++}$ 0.69 × $10^{-6}$. In these forms the metal is evidently held by chelation between the O atom in the 8-position and at the N atom of the azo group. The azo deriv. from 7-bromo-8-hydroxyquinoline and $PhN_2Cl$ must have the azo group at 5-position. Thie dye does not form complexes (colors or ppts.) with the above divalent metal salts; this dye, however is an indicator and gives red color in acids, probably due to quinone-hydrazone tautomeric form; addn. of Cu salt soln. destroys the red color and changes it to yellow, similar to that of the above complexes. Spectra of the complexes are shown. G. M. Kosolapoff

**Ring enlargement. The Schmidt reaction on 1-hydrindanone.** Giorgio Di Maio and Paolo Antonio Tardella (Univ. Rome). *Gazz. Chim. Ital.* 91, 1345–51(1961). Hydrindanone (I) (1.1 g.) in 10 ml. $CHCl_3$ treated with 3 ml. $H_2SO_4$, to the mixt. 0.63 g. $NaN_3$ added portionwise with stirring and cooling, the mixt. stirred 1 hr., basified, extd. with $CHCl_3$, the exts. washed with $H_2O$, dried ($Na_2SO_4$), and the solvent evapd. gave 0.98 g. residue (II). A sample of II was kept under high vacuum to remove the unreacted I, then sublimed at 90°/0.04 mm. and the sublimate (III) submitted to infrared spectral detn. II was chromatographed ($Al_2O_3$) with $C_6H_6$–$CHCl_3$ as eluent to give *trans*-octahydrocarbostyril (IV), m. 145–7° ($Et_2O$), as first fraction, then *cis*-octahydroisocarbostyril (V), m. 147–51° ($Et_2O$), and finally *trans*-octahydroisocarbostyril (VI), m. 197–8° ($CHCl_3$–$Et_2O$). The presence of about 20% of *cis*-octahydrocarbostyril (VII) in III was proved by comparison of the infrared spectrum of III with that of a mixt. of 22.5% VII, 38.5% IV, 29% V, and 10% VI. G. Cignarella

**Search for new trypanocides. VII. *m*-Amidinophenyldiazoaminostyrylquinolinium salts.** S. S. Berg (May & Baker Ltd., Dagenham, Engl.). *J. Chem. Soc.* 1962, 677–9; cf. *CA* 56, 4759*a*. Diazotized 2- and 4-aminostyrylquinolinium salts coupled with *m*-aminobenzamidine-HCl (I) to give diazoamino compds. possessing significant babesicidal and trypanocidal activity. 1,2-Dimethylquinolinium Me sulfate (78 g.), 49 g. *p*-acetamidobenzaldehyde, 5 ml. piperidine, and 250 ml. alc. refluxed overnight, the salt collected, washed, and recrystd. gave 101 g. 2-(4-acetamidostyryl)-1-methylquinolinium Me sulfate (II), orange needles, m. 297–8° (decompn.). Compds. similarly prepd. were: 2-(3-acetamidostyryl)-1-methylquinolinium Me sulfate, 61% yield, m. 240–2°, and 4-(4-acetamidostyryl)-1-methylquinolinium Me sulfate, 74%, m. 274–5° (decompn.). 4-Acetamidoquinaldine (20 g.) heated 1 hr. with 10 ml. $Me_2SO_4$ in 200 ml. anhyd. $PhNO_2$ gave 25 g. 4-acetamido-1,2-dimethylquinolinium Me sulfate (III), prisms, m. 219–20° (alc.). III (38 g.), 20 g. *p*-acetamidobenzaldehyde, 1.6 ml. piperidine, and 100 ml. alc. refluxed 1 hr., filtered, the solid washed, dissolved in 1.2 l. hot $H_2O$, and treated with 600 ml. satd. NaCl gave 27 g. 4-acetamido-2-(4-acetamidostyryl)-1-methylquinolinium chloride, orange needles, m. 294° (decompn.). II (20 g.) refluxed 2 hrs. with 200 ml. 5*N* HCl, cooled, the solid filtered off, and crystd. gave 13.2 g. 2-(4-aminostyryl)-1-methylquinolinium chloride-HCl, orange needles, m. 252° (decompn.). Similar reactions gave: 88% 2-(3-aminostyryl)-1-methylquinolinium chloride-HCl, m. 262–4° (decompn.); 98% 4-(4-aminostyryl)-1-methylquinolinium chloride-HCl, red prisms, m. 278° (decompn.); 96% 4-amino-2-(4-aminostyryl)-1-methylquinolinium chloride-HCl, yellow prismatic needles, m. 304° (decompn.). The aminostyrylquinolinium salt (0.1 mole) in 600 ml. *N* HCl diazotized at 5–8° by addn. of 75. g. $NaNO_2$, the mixt. stirred 1 hr. at 5–8°, treated with $H_2SO_4$, 21 g. I in 40 ml. 2*N* HCl and 60 ml. $H_2O$ added rapidly, followed by slow addn. of 105 g. NaOAc in 305 ml. $H_2O$, the soln. stirred 1 hr. at 5–10°, 51 g. NaCl added, the solid filtered, washed, and crystd. The following 2(or 4)-[3(or 4)-(*m*-amidinophenyldiazoamino)styryl]-1-methylquinolinium chloride-HCl were thus obtained (R substituent, crystn. solvent, m.p. of product, and % yield given): H, 60% aq. alc., 229°, 70; H, aq. alc., 217°, 37; $NH_2$, aq. alc., 238–40°, 58. 4-[3-(*m*-Amidinophenyldiazoamino)styryl]-1-methylquinolinium chloride-HCl, 53%, m. 238° (MeOH–$Me_2CO$). B. K. Wasson

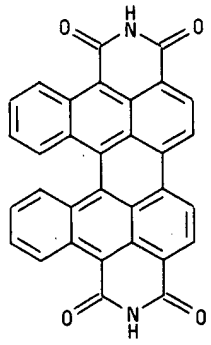
**Reissert compound studies. II. Nature of the quinoline.** Frank D. Popp, Wm. Blount, and Perry Melvin (Univ. of Miami, Coral Gables, Fla.). *J. Org. Chem.* 26, 4930–2(1961); cf. *Chem. & Ind.* (London) 550(1961). Reaction of a wide variety of 3-, 4-, 5-, 6-, and 7-substituted quinolines with BzCl and KCN in $CH_2Cl_2$–$H_2O$ resulted in the formation of the appropriate Reissert compds. The yields of Reissert compds. were largest when the substituents were electron-donating groups. No Reissert compds. could be obtained from 2- and 8-substituted quinolines. With one exception all the Reissert compds. gave BzH on acid catalyzed hydrolysis. Method *A*. KCN (0.048 mole) in 25 ml. $H_2O$ was treated with 0.16 mole of the quinoline, 0.032 mole BzCl added in 2 hrs., stirred 2 hrs., the solid or oil collected, washed, and then recrystd. from the appropriate solvent. Method *B*. BzCl (0.032 g.) was added in 2 hrs. to a mixt. of 0.016 mole of the quinoline in 20 ml. $CH_2Cl_2$, stirred 6–8 hrs. with 0.048 mole KCN in 8 ml. $H_2O$, washed, dried, evapd., and the product sepd. If the product was an oil it could be crystd. by treatment with the appropriate solvent. The following quinoline Reissert compds. were thus obtained (substituent, m.p., % yield by method *A* and method *B*, and the % BzH obtained by hydrolysis given): 3-acetamido, 160–1°, 50, 15, 89; 3-$NH_2$, 169–70°, 68, 0, 46; 3-Br, 125°, 15, 0, 93; 3-OH, 179–80°, 58, —, 0; 4-MeO, 173–5°, 71, trace, 87; 4-OH, 157–8°, 98, 0, 86; 4-Cl, 141°, 33, —, 92; 4-MeO, 146°, 82, —, 86; 5-$NH_2$, 187–8°, 63, 0, 99; 5-$NO_2$, 162–3°, 19, —, 10; 5-OH, 172–3°, 99, —, 99; 5-$CO_2Me$, 116–17°, 61, —, 93; 6-Me, 144°, 99, 52, 90; 6-Br, 165–6°, 48, 40, 93; 6-$NH_2$, 195°, 95, —, 96; 6-MeO, 126°, 89, 88, 95; 6-$NO_2$, 200–1°, 29, 0, 43; 6-OH, 188°, 99, 0, 75; 6-$NMe_2$, 176°, 59, 0, 93; 6-$CO_2Me$, 115°, 49, —, 99; 7-Me, 164–5°, 64, 54, 84; 7-OH, 126–7°, 89, —, 99; 7-$NO_2$, 185°, 17, —, 16; 4,6-$Me_2$, 130–1°, 94, 0, —; 7,4-Cl(HO), 171–2°, 20, —, 20; 4,7-$Cl_2$, 155°, 34, 0, 77; 4,6-Cl(MeO), 167–8°, 87, —, 48; 5,6-benzo, 182°, 94, 43, 84. The acid hydrolysis was accomplished by adding 11 ml./0.5 g. Reissert compd. of concd. HCl to an equimolar mixt. of Reissert compd. and 2,4-dinitrophenylhydrazine, and the mixt. heated 0.5 hr., left 2 days at room temp., and the amt. of 2,4-dinitrophenylhydrazone of BzH detd. B. K. Wasson

**Reissert compds. III. Nature of the isoquinoline.** Frank D. Popp and William Blount (Univ. of Miami, Coral Gables, Fla.). *J. Org. Chem.* 27, 297–8(1962); cf. preceding abstr. Substituted isoquinolines (I) [R = substituent(s)] including 1-methylisoquinoline (II) were treated with BzCl and KCN in $CH_2Cl_2$–$H_2O$ to give Reissert compds., substituted 2-benzoyl-1-cyano-1,2-dihydroisoquinolines (III) [R = substituent(s)]. Substances giving the correct analysis for Reissert compds. were also obtained from 1-azapyrene (IV) and 2-azafluoranthene (V). IV, BzCl, and KCN in $CH_2Cl_2$–$H_2O$ yielded 54% solid, m. 212–13° (alc.), hydrolyzed in concd. HCl in the presence of 2,4-$(O_2N)_2$-$C_6H_3NHNH_2$ to give 2,4-$(O_2N)_2C_6H_3NH$:CHPh. Similarly V yielded 23% solid, $C_{28}H_{14}N_2O$, m. 158–9° (alc.). Data on formation of III are listed (R, m.p./solvent, % yield by $CH_2Cl_2$–$H_2O$ and $H_2O$ methods, and % yield BzH on hydrolysis given): H, 125–6°/alc., 69, 72, 95; 4-$H_2N$, 158°/80% alc., 20, —, 90; 4-Br, 173°/alc., 38, 0, 90; 5-OH, 198°/alc., 68, —, 90: 5-$O_2N$, 148°/alc., 10, 0, 12; 8-$O_2N$, 181°/alc., 9, —, 9; 3,5-Me(NC), 175°/80% alc., 45, —, 97; 3,5-Me($O_2N$), 159°/80% alc., —, —, 63; 3,8-Me($O_2N$), 134°/75% iso-PrOH, 28, —, 85; 5-$CO_2Me$, 121°/80% alc., 29, —, 98. Formation of III from V was unexpected in view of the failure of III to react. C. R. Addinall

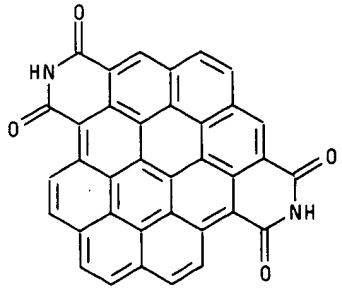
**Steric requirements for ganglionic blockade: synthesis of certain [quinolinic] acetylenic diamines and their derivatives.** John L. Neumeyer (Univ. of Wisconsin, Madison). *Univ. Microfilms* (Ann Arbor, Mich.), *Order No.* 62-1189, 68 pp.; *Dissertation Abstr.* 22, 3001(1962). CA

**Chemical constitution of enmein, a bitter principle from Isodon trichocarpus.** Takashi Kubota, Teruo Matsuura, Tsutomu Tsutsui, and Keizo Naya (Osaka City Univ.). *Bull. Chem. Soc. Japan* 34, 1737–8(1961). The structure of enmein, $C_{20}H_{26}O_6$, m. 274–5, $[\alpha]_D$ −156° (acetone), was proposed as I on the basis of information previously presented (Ikeda and Kanatoma, *CA* 53, 3389*a*; Takahashi, *et al.*, *CA* 55, 2590*d*). The structure was supported by catalytic hydrogenation and subsequent analysis of its decompn. products by ultraviolet and nuclear magnetic

L14 ANSWER 3 OF 33 ZCAPLUS COPYRIGHT 1998 ACS
AN 1995:546010 ZCAPLUS
DN 122:316901
TI Design and synthesis of near-infrared absorbing pigments. I. Use of Pariser-Parr-Pople molecular orbital calculations for the identification of near-infrared absorbing pigment candidates
AU Desilets, Denis; Kazmaier, Peter M.; Burt, Richard A.
CS Xerox Res. Cent. Canada, Mississauga, ON, L5K 2L1, Can.
SO Can. J. Chem. (1995), 73(3), 319-24
CODEN: CJCHAG; ISSN: 0008-4042
DT Journal
LA English
IT ***6424-79-9D*** , *N,N'*-dialkyl derivs. ***163657-24-7D*** , *N,N'*-dialkyl derivs. ***163657-26-9D*** , *N,N'*-dialkyl derivs. ***163657-30-5D*** , *N,N'*-dialkyl derivs. ***163685-87-8D*** , *N,N'*-dialkyl derivs.
(PPP MO calcns. for identification of near-IR-absorbing pigment candidates)
RN 6424-79-9 ZCAPLUS
CN Dibenzo[*h,h'*]phenanthro[2,1,10-*def*:7,8,9-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetrone (9CI) (CA INDEX NAME)



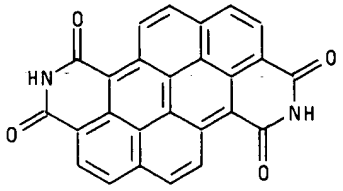
RN 163657-24-7 ZCAPLUS
CN Ovaleno[1,14-*cd*:6,7-*c'd'*]dipyridine-1,3,10,12(2*H*,11*H*)-tetrone (9CI) (CA INDEX NAME)



RN 163657-24-7 ZCAPLUS

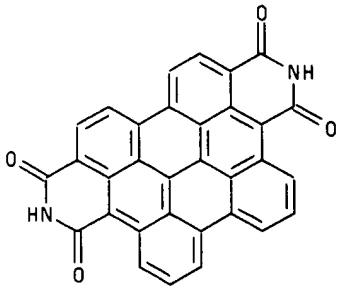
RN 163657-26-9 ZCAPLUS

CN Pyreno[9,10,1-*def*:4,5,6-*d'e'f'*]diisoquinoline-3,5,10,12(4*H*,11*H*)-tetrone (9CI) (CA INDEX NAME)



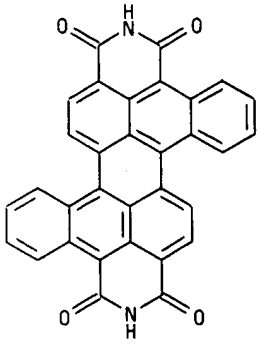
RN 163657-30-5 ZCAPLUS

CN Dibenzo[3,4:5,6]pyreno[2,1,10-*def*:7,8,9-*d'e'f'*]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetrone (9CI) (CA INDEX NAME)



RN 163685-87-8 ZCAPLUS

CN Dibenz[*h*,*h'*]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetrone (9CI) (CA INDEX NAME)



(PPP MO calcns. for identification of near-IR-absorbing pigment candidates

AB The usefulness of the PPP MO method for the identification of near-IR absorbing pigment

L5 ANSWER 7 OF 8 BEILSTEIN COPYRIGHT 1998 BEILSTEIN CD&S

Note(s):

4. Handbook Data

PRE

Start: anthracene-dicarboxylic acid-(1.9)-monoamide

Detail: Ansaeuern der alkalischer Loesung mit starken Mineralsaeuern

Reference(s):

1. Patent: Kardos, D.R.P. 282711
   Friedlaender, 12,487
2. Kardos, Chem.Ber., 46 <1913>,2088, CODEN: CHBEAM

Note(s):

3. Handbook Data

PRE

Start: aceanthrenequinone monoxime

Reag: concentrated sulfuric acid

Reference(s):

1. Patent: Kardos, D.R.P. 282711
   Friedlaender, 12,487
2. Kardos, Chem.Ber., 46 <1913>,2087,2089, CODEN: CHBEAM

Note(s):

3. Handbook Data

PRE

Start: BRN=17931 anthracene-1,9-dicarboxylic acid-anhydride

Reag: ammonium acetate, NH3

Time: 2 hour(s)

Yield: 80.00 %

Temp: 110.0 Cel

Reference(s):

1. Desilets, Denis; Kazmaier, Peter M.; Burt, Richard A.; Hamer, Gordon K., Can.J.Chem., 73 <1995> 3, 325-335, LA: EN, CODEN: CJCHAG

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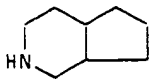
L18 ANSWER 9 OF 19 COPYRIGHT 1997 ACS
AN CA59:15253d CAOLD
IT ***54152-52-2***
RN 54152-52-2 CAOLD
CN 1*H*-Cyclopenta[*c*]pyridine, octahydro- (9CI) (CA INDEX NAME)

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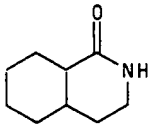
L18 ANSWER 10 OF 19 COPYRIGHT 1997 ACS
AN CA57:781d CAOLD
IT ***20597-65-3***
RN 20597-65-3 CAOLD
CN Isocarbostyril, octahydro- (6CI, 7CI, 8CI) (CA INDEX NAME)

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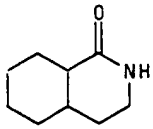
L18 ANSWER 11 OF 19 COPYRIGHT 1997 ACS
AN CA56:15483c CAOLD
IT ***20597-65-3***
RN 20597-65-3 CAOLD
CN Isocarbostyril, octahydro- (6CI, 7CI, 8CI) (CA INDEX NAME)

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RN 163685-87-8 ZCAPLUS

candidates for photogenerator applications is outlined. Several pigments based on the well known class of photogenerating N,N'-dialkyl-3,4,9,10-perylenetetracarboxylic diimides were investigated and pigments of the dibenzoperylene, bisanthene, and zethrene classes were identified as the most promising candidates of the series. On the basis of the predictions, 7,8,15,16-dibenzo[a,j]perylenetetracarboxylic diimide was prepd. and the validity of the calcns. was verified.

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L14 ANSWER 4 OF 33 ZCAPLUS COPYRIGHT 1998 ACS

AN 1995:353298 ZCAPLUS

DN 122:187526

TI Synthesis of quinazoline-2,4-dione and naphthalimide derivatives as new 5-$HT_3$ receptor antagonists

AU Langlois, M.; Soulier, J. L.; Rampillon, V.; Gallais, C.; Bremont, B.; Shen, S.; Yang, D.; Giudice, A.; Sureau, F.

CS Fac. De Pharmacie, CNRS, Chatenay-Malabry, 92296, Fr.

SO Eur. J. Med. Chem. (1994), 29(12), 925-40
CODEN: EJMCA5; ISSN: 0223-5234

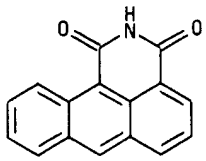
DT Journal

LA English

IT ***161500-03-4***
(prepn. and 5-$HT_3$ receptor antagonist activity of quinazolinediones, benzisoquinolinones, and -diones)

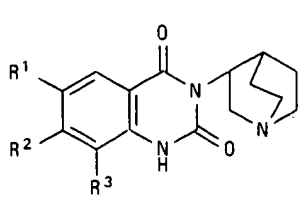
RN 161500-03-4 ZCAPLUS

CN 1*H*-Dibenz[*de*,*h*]isoquinoline-1,3(2*H*)-dione (9CI) (CA INDEX NAME)

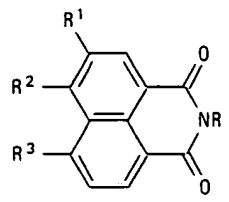


GI

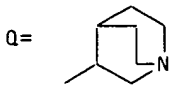
RN 161500-03-4 ZCAPLUS

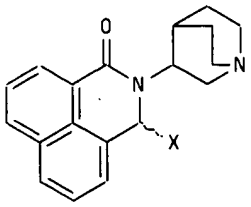


I



II





III

AB New potent 5-$HT_3$ receptor antagonists, quinazolidinediones **I** ($R^1$ = H, Cl, Br, iodo, $R^2$ = H, Cl, $NO_2$, $NH_2$, $R^3$ = H, Me), benzisoquinolinediones **II** (R = Q, $Q^1$, etc., $R^1$ = H, $NO_2$, $CHMe_2$, etc., $R^2$ = H, Cl, Br, $NO_2$, etc., $R^3$ = H, $R^2R^3$ = $CH_2CH_2$), and benzisoquinolinones **III** (X = OMe, H), have been designed from the naphthalimide moiety and a quinuclidine heterocycle and the structure-activity relationships are discussed here on the basis of the nature of the substituent on the arom. system. The biol. activity of the compds. was evaluated in binding assays with [$^3$H]BRL-43694 and by inhibition of the Bezold-Jarisch reflex. **II** (R = Q, $R^1$ = $R^3$ = H, $R^2$ = $NH_2$) (**IV**) with a 4-amino substituent was equipotent to the ref. compds. In contrast to the benzamide derivs., the activity resides essentially in the (R) enantiomer ($K_i$ = 0.15±0.05nM, $ID_{50}$ = 1,6$\mu$g/kg/i.v.) and it is demonstrated that the addnl. carbonyl group is involved in the inversion of the enantioselectivity of the receptor. Conformational studies of (R)-**IV** demonstrated the presence of a locked structure with 4-minimal energy conformers which were compared to those of (S)-zacopride. The superimposition of the putative active conformers emphasized the presence of a second polar group in the binding site. The fluorescent properties of the compds. were studied and indicate that (R)-**IV** and its derivs. may be promising tools for the direct visualization of 5-$HT_3$ receptors.

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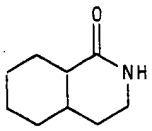
L18 ANSWER 18 OF 19 COPYRIGHT 1997 ACS
AN CA52:14606i CAOLD
IT ***20597-65-3***
RN 20597-65-3 CAOLD
CN Isocarbostyril, octahydro- (6CI, 7CI, 8CI) (CA INDEX NAME)

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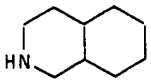
L18 ANSWER 19 OF 19 COPYRIGHT 1997 ACS
AN CA51:10527h CAOLD
IT ***6329-61-9***
RN 6329-61-9 CAOLD
CN Isoquinoline, decahydro- (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)




**********

52: 14606 c-f -26-



similarly reduced, but with the addn. of 1.1 cc. concd. $H_2SO_4$, absorbed 2.3–2.5 moles H to yield 2.6 g. 5,6,7,8-tetrahydro deriv. (VIII) of III, m. 82° (petr. ether) (picrate, m. 268°; HCl salt, m. 228°), together with 1.6 g. 1-amino-decahydroisoquinoline monoacetate, m. 186° ($Me_2CO$); *a* picrate, m. 210°. VIII (0.65 g.) in 36 cc. 19% $H_2SO_4$ diazotized by 0.33 g. $NaNO_2$, the mixt. kept 1 hr. in the cold, made alk., and extd. with $CHCl_3$ yielded 0.58 g. VII. The structure of VIII was confirmed by its conversion according to Grewe, *et al.* (*C.A.* 44, 1994*f*), through the diazo compd. to the corresponding Br deriv., m. 48° (picrate, m. 105°), which was catalytically reduced to the 5,6,7,8-tetrahydro deriv. of IV. VII (1 g.) heated 3 hrs. at 130° with 20 cc. $POCl_3$ in a sealed tube, the cooled mixt. treated *b* with ice, made alk., and extd. with ether yielded 0.9 g. VI (halo = Cl), $b_6$ 120–5°, m: 19–20°; picrate, m. 97–9°. Thus, a sure method with good yields was developed for the prepn. of the VI in 4 steps from III or in 3 steps from V.

H. S. French

Synthesis of 2,6-lutidine from methyl vinyl ketone. Makoto Tanaka and Niro Murata (Osaka Prefect. Univ., Sakai). *Kōgyō Kagaku Zasshi* 59, 1181–3(1956).—3-Carbethoxy-2,6-heptanedione (I), $b_{2.5}$ 111–12°, prepd. from *c* $MeCOCH:CH_2$ (II) by Michael reaction with $AcCH_2CO_2Et$ and MeONa in 88% yield, was converted to 2,6-lutidine (III) by the following 4 procedures. I was treated with $NH_3$ in EtOH to give white crystals, m. 70–80°, which gave Et 2,6-dimethylnicotinate (IV) by oxidation with air at 100–110° 24 hrs. in 59% yield to II. IV was sapond. in EtOH with KOH by boiling 2 hrs. followed by heating with CaO and distn. to give III. 2,6-Heptanedione (V), produced by decompn. of I at 500–20° in N, was treated with $NH_3$ in EtOH, oxidized with air in xylene at 120–30° 20 hrs., *d* and then extd. with $CHCl_3$ with $NH_4OH$ added to give 26% III. I (1 mole) with 1 mole hydroxylamine-HCl in $H_2O$ with 0.5 mole $Na_2CO_3$ added at the b.p. 5 hrs. gave III by extn. with $CHCl_3$ and distn. in 33% yield to I. Decompn. of I with $H_2SO_4$ by boiling several hrs. gave only a slight amt. of III.

Katsuya Inouye

The preparation of β-lactams by addition of ketenes to $\Delta^2$-thiazolines and Schiff bases. Robert Pfleger and Alfred Jäger (Univ. Erlangen, Ger.). *Chem. Ber.* 90, 2460–70 *e* (1957).—Reactions of $Ph_2C:CO$ (I), $PhCH:CO$ (II), and $CH_2:CO$ (III) with 2-substituted thiazolines and with azomethines are examd. to det. the influence of substituents on β-lactam formation. The addns. are hindered by *o*- or *p*-Cl or *o*-, *m*-, or *p*-$NO_2$ groups in either ring of PhCH:NPh, but favored by *m*-Cl or *p*-$Me_2N$ groups. $Me_2CHCH_2CH$:NPh and $PhCH_2N:CHPh$ failed to react with I. I was prepd. separately and added to the reaction mixt. in EtOAc or $C_6H_6$ or without solvent. II was prepd. *in situ* from *f* $BzCHN_2$ and freshly prepd. $Ag_2O$, and III was introduced as gas. Compds. which did not react without catalyst (up to 200°) did not do so in the presence of $BF_3$, $AlCl_3$, $ZnCl_2$, or $FeCl_3$. 2-Mercaptothiazoline (IV) (0.6 g.) and 0.97 g. I shaken 20 min. in an N atm. with 13 cc. EtOAc pptd. 68% *β-lactam of 2-(diphenylacetylthio)thiazolidine-2-(α,α-diphenylacetic acid)*, m. 182°. This is hydrolyzed by aq. MeOH-NaOH to $Ph_2CHCO_2H$ and IV, and by $PhNH_2$ (2 min. at 100°) to $Ph_2CHCONHPh$. IV gave no product *g* with II (to 80°) or III (to 200°). 2-Aminothiazoline (V) with I gives first *2-(diphenylacetamido)thiazoline*, m. 193°, then the *β-lactam of 2-(diphenylacetamido)thiazolidine-2-(α,α-diphenylacetic acid)*, m. 125° (or 147°) (sic). V failed to react with II or III. 2-Acetamidothiazoline with I gave 54% (or 44%) (sic) *β-lactam of 2-(acetamidothiazolidine)-2-(α,α-diphenylacetic acid)*, m. 147° (or 125°) (sic). 2-Phenyl-5,5-dimethyl-4-(carbomethoxy)thiazoline did not react with I. The following were prepd. *1,3,3-Triphenyl-4-arylazetidin-2-ones* from I and ArCH:NPh (VI) (4-substituent, % yield, reaction temp., and m.p. given): *o*-Me, 52, 70–80°, 168°; *m*-Me, 63, 70–80°, 107.5°; *p*-Me, 72, room temp., 171°; *o*-MeO, 30, 70–80°, 236°; *m*-MeO, 21, 150°, 240°; *m*-Cl, 71, room temp., 176.5°; *p*-$Me_2N$, 67, room temp., 173.5°. *1-Aryl-3,3,4-triphenylazetidin-2-ones*, from I and PhCH:NAr (VII) at room temp. (4-substituent, % yield, and m.p. given): *o*-Me, 72, 165°; *m*-Me, 69, 166.5°; *p*-Me, 21, 169°; *o*-MeO, 55, 150°; *p*-MeO, 16, 204°; *m*-Cl, 98, 183°. *1,3-Diphenyl-4-arylazetidin-2-ones* *i* from II and VI at 40–50°: H, 35, 133°; *o*-Me, 21, 138°; *m*-Me, 20, 129°; *p*-Me, 14, 117.5°; *o*-MeO, 25, 124°; *m*-MeO, 29, 136°; *m*-Cl, 13.5, 131°; *p*-$Me_2N$, 90, 153°. *1-Aryl-3,4-diphenylazetidin-2-ones* from II and VII at 40–50°: *o*-Me, 12, 143°; *m*-Me, 15, 133°; *p*-Me, 15, 180°; *o*-MeO, 5, 139°; *p*-MeO, 19, 156°; *m*-Cl, 28, 123°. *1-Phenyl-4-arylazetidin-2-ones* from III and VI at 180–200°: *o*-Me, 11.5, 134°; *m*-Me, 12, 87°; *p*-Me, 22, 109°; *o*-MeO, 39, 108°; *m*-MeO, 16, 96°; *m*-Cl, 32, 148°; *p*-$Me_2N$, 62, 155°. *1-Aryl-4-phenylazetidin-2-ones* from III and VII at 180–200°: *o*-Me, 7, 107°; *m*-Me, 18, 91°; *p*-Me, 13, 126°; *p*-MeO, 19, 86°; *m*-Cl, 34, 97°. *o*- and *p*-Cl, and *o*-, *m*-, and *p*-$NO_2$ derivs. of VI and VII failed to react with I (to 200°) or II (to 80°); *o*-$PhCH:NC_6H_4$-OMe failed to react with III. PhN:CMeCMe:NPh (VIII) and $PhCH:CHCH:NPh$ (IX) react by 1,4-addn. VIII with I (3 hrs. boiling in EtOAc) gives 61% *1,3,3,4-tetraphenyl-5,6-dimethyl-2-oxo-1,2,3,4-tetrahydropyrazine*, m. 187°, and with II gives 47% *1,3,4-triphenyl-5,6-dimethyl-2-oxo-1,2,3,4-tetrahydropyrazine*, m. 122°. IX with II gives 32% *1,3,4-triphenyl-3,4-dihydro-2-pyridinone*, m. 107°, and with III gives 69% *1,4-diphenyl-3,4-dihydro-2-pyridinone*, m. 87°. VIII failed to react with III. II and $Ph_2C:NPh$ heated 4 hrs. in $C_6H_6$ at 40–50° give 42% *1,3,4,4-tetraphenylazetidin-2-one*, m. 153°.

M. A. Simkins

Identification of 2-naphthyl-1-methylimidazole and diphenylpiperidinepropane. Detlef Horn (Inst. Arzneimittelprüfung, Jena, Ger.). *Pharm. Zentralhalle* 93, 182–5 (1954).—With Marquis reagent ($HCHO-H_2SO_4$) 2-naphthyl-1-methylimidazole (I) gives an intense steel-blue color reaction and diphenylpiperidinepropane (II) an intense red color. For a quant. colorimetric detn., 0.5–2.5 mg. I or II in soln. was evapd. to dryness and the residue taken up in 0.5 ml. 1% HCHO, 25 ml. $H_2SO_4$ was added, mixed well, and the red color formed within 3 min. detd. at 660 mμ for I and between 465–496 mμ for II. Both compds. gave a straight line for values plotted using 0.5–2.5 mg.

B. Prytz

Preparation and chemistry of the complexes of 2,5-di-(α-pyridyl)pyrrole. Fr. Hein and Ursula Beierlein (Friedrich-Schiller Univ., Jena, Ger.). *Pharm. Zentralhalle* 96, 401–21(1957).—α-Picoline (93 g.) in 200 ml. $H_2O$ heated to 80° with stirring under reflux, 2 moles $KMnO_4$ added portionwise but waiting after each addn. until the temp. returned to 80°, heated 0.5 hr. more on the boiling $H_2O$ bath with const. vigorous stirring, the mixt. filtered hot, the ppt. washed several times with hot $H_2O$, and the cooled filtrate treated with satd. $Cu(OAc)_2$ soln. gave 90–100 g. Cu picolinate (I). I was converted to picolinic acid (II) HCl salt (IIa) by the method of Meyer [*Monatsh. Chem.* 23, 438(1902)]. IIa (39 g.), 80 g. abs. EtOH, 160 ml. abs. $C_6H_6$, 30 g. $MgSO_4$, and 19 g. concd. $H_2SO_4$ refluxed 5 hrs. in a Soxhlet app. (the $MgSO_4$ was contained in the Soxhlet shell) gave 13 g. II Et ester (III). III treated according to Gilman and Broadbent (*C.A.* 42, 8782*b*) gave 70–5% Na (pyridoylethyl)acetate (IV). IV (2 moles) condensed with 2 g.-atoms iodine gave di-Et dipyridoylsuccinate which was cyclized with $NH_4OAc$-HOAc to 2,5-di(α-pyridyl)pyrrole-3,4-dicarboxylic acid (V) di-Et ester (VI) and hydrolyzed to V. V (4 g.) in 10 g. freshly distd. $H_2NCH_2CH_2OH$ boiled 1.5 hrs. on the sand bath, cooled, run into 300 ml. $H_2O$ with vigorous stirring, kept overnight, and the ppt. filtered off and washed gave 2.61 g. crude 2,5-di(α-pyridyl)pyrrole (VII), crystd. from MeOH-$H_2O$ or $Me_2CO$-$H_2O$ to give VII, m. 96°; *di-HCl salt*, decomp. 208–12°; *dinitrate*, m. 175° (decompn.). The next 2 prepns. were carried out under highly purified N, the solvents boiled out with N, and then cooled and kept under N. $Fe(OAc)_2$ (prepd. under N) (0.5 g.) in 25 ml. air-free $H_2O$ filtered through kieselguhr into 1 g. finely powd. VI in 74 ml. O-free EtOH, let stand, the ppt. filtered off, washed 3 times with 60–80% air-free EtOH-$H_2O$, and dried gave 800 mg. Fe(II) complex, recrystd. from abs. EtOH under N to yield needles, m. 208°. Similarly was prepd. the Cr(II) complex. The following complexes of VII were prepd. (metal complexed and m.p. given): Co(II), 273–4°; Ni(II), 318°; Fe(II), 168°; Zn, —; Cu(II) (which combined with 3 moles of VII), 155–6°; Ag(I), 214°. $FeCl_3$ and VII formed a *complex*, decomp. 265°.

William Braker

Syntheses of piperazines. IX. Stereoisomers of 2,3-dimethylpiperazine. Takeo Ishiguro, Eiichi Kitamura, Masaki Matsumura, and Masaaki Awamura (Univ. Kyoto). *Yakugaku Zasshi* 78, 338–41(1958); cf. *C.A.* 52, 11862*a*—α-2,3-Dimethylpiperazine (I) (2.85 g.) in 30 ml. $Me_2CO$ treated with 11.6 g. *d*-α-camphorsulfonic acid (II) in 80 ml. $Me_2CO$ and the product filtered gave 14.1 g. *α-d-I α-camphorsulfonate* (III), needles, m. 317–22°, $[\alpha]_D^{19}$ 18.5°; III treated

RN 73975-15-2 ZCAPLUS

Diels-Alder reaction of **III** with fumaronitrile gave **I** (R = $R^2$ = cyano, $R^1$ = H). **III** was aromatized, the Diels-Alder adduct of 2-(1-naphthyl)furan with $MeO_2CC{:}CCO_2Me$ was prepd. and converted to di-Me 3-hydroxy-6-(1-naphthyl)phthalate (**IV**), **IV** was heated with polyphosphoric acid to yield **II**, and **II** reacted with $N_2H_4$ to give a phenalenophthalazinone deriv.

**********

L14 ANSWER 10 OF 33 ZCAPLUS COPYRIGHT 1998 ACS

AN 1980:22393 ZCAPLUS

DN 92:22393

TI 1-Amino-4-phenylisoquinoline derivatives

IN Simmonds, Robin George

PA Aspro-Nicholas Ltd., Engl.

SO Brit., 16 pp.
CODEN: BRXXAA

DT Patent

LA English

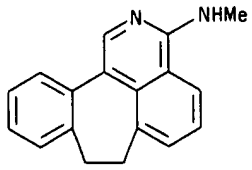
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|---|---|---|---|---|
| PI | GB1545767 | A | 19790516 | 75GB-0031144 | 19760630 |

IT ***72240-23-4P*** ***72240-24-5P***
(inflammation inhibitor, prepn. of)

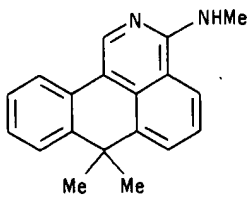
RN 72240-23-4 ZCAPLUS

CN Benzo[6,7]cyclohept[1,2,3-*de*]isoquinolin-3-amine, 7,8-dihydro-*N*-methyl- (9CI) (CA INDEX NAME)




RN 72240-24-5 ZCAPLUS

CN 7*H*-Dibenz[*de*,*h*]isoquinolin-3-amine, *N*,7,7-trimethyl- (9CI) (CA INDEX NAME)

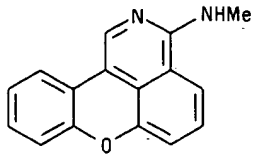


RN 72240-24-5 ZCAPLUS

IT ***72240-21-2P*** ***72240-22-3P*** ***72240-27-8P***
(prepn. and central nervous system activity of)

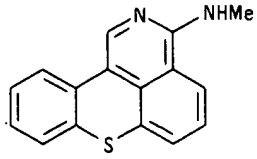
RN 72240-21-2 ZCAPLUS

CN [1]Benzopyrano[4,3,2-*de*]isoquinolin-3-amine, *N*-methyl- (9CI) (CA INDEX NAME)



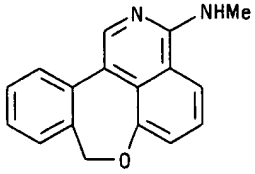

RN 72240-22-3 ZCAPLUS

CN [1]Benzothiopyrano[4,3,2-*de*]isoquinolin-3-amine, *N*-methyl- (9CI) (CA INDEX NAME)




RN 72240-27-8 ZCAPLUS

CN 8*H*-[2]Benzoxepino[5,4,3-*de*]isoquinolin-3-amine, *N*-methyl- (9CI) (CA INDEX NAME)




IT ***72240-26-7P***
(prepn. of)

RN 72240-26-7 ZCAPLUS

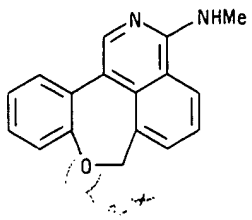
CN 7*H*-[1]Benzoxepino[5,4,3-*de*]isoquinolin-3-amine, *N*-methyl-, (2*Z*)-2-butenedioate (1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 72240-25-6

CMF $C_{17}H_{14}N_2O$

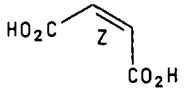
RN 72240-26-7 ZCAPLUS



CM 2

CRN 110-16-7
CMF $C_4H_4O_4$
CDES 2:Z

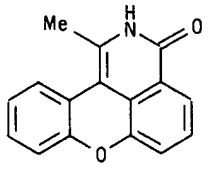
Double bond geometry as shown.



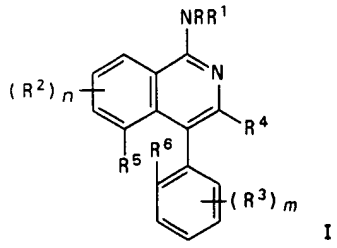
IT ***72240-50-7P***
(prepn. of, as intermediate in benzopyranoisoquinoline prepn.)

RN 72240-50-7 ZCAPLUS

CN [1]Benzopyrano[4,3,2-*de*]isoquinolin-3(2*H*)-one, 1-methyl- (9CI) (CA INDEX NAME)



GI



I

RN 72240-50-7 ZCAPLUS

AB The prepn. is described of title compds. **I** (R, $R^1$ = H, $C_{1-12}$ alkyl; $RNR^1$ = piperazinyl optionally substituted by $C_{1-12}$ alkyl or hydroxyalkyl; *n* = 0 - 3; *m* = 0 - 4; $R^2$,$R^3$ = $C_{1-12}$ alkyl optionally substituted by ≥1 halo, $C_{1-12}$ alkoxy, halo; $R^4$ = H, $C_{1-12}$ alkyl; $R^5$,$R^6$ = H or $C_{1-12}$ alkyl, alkylthio, alkoxy; $R^5R^6$ = bond, O, S, $C_{1-3}$ alkylene optionally contg. ≥1 O or S), which show antiinflammatory (esp. antirheumatic) and/or central nervous system activity. Thus, 3-dimethylamino-7,8-dihydrobenzo[1,2]cyclohepta[3.4.5-*de*]isoquinoline hydrogen maleate was prepd. from dibenzo[*ad*]suberone by sequential treatment with $NaH/Me_3S^+ I^-$, $BF_3.Me_2O/CH_2Cl_2$, and $H_2NCO_2Et/H_2SO_4$ followed by heating (256°, 1 h), refluxing with $POCl_3$, and $Me_2NH$/EtOH treatment. The yields of the 6 steps were 96, 98, 100, 89, 99, and 75.6%, resp. Compns. contg. **I** are described.

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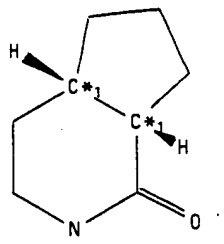
L18 ANSWER 9 OF 10 COPYRIGHT 1997 BEILSTEIN CD&S

D5

| | |
|---|---|
| Beilstein Reg. No. (BRN): | 1447527 Beilstein |
| Molecular Formula (MF): | C8 H13 N O |
| Synonym (SY): | cis-3,4-Trimethylen-piperidon-(2) |
| Autonom Name (AUN): | octahydro-<2>pyrindin-1-one |
| Beilstein Reference (SO): | 5-21-07-00050 |
| General Comments (NTE): | Stereo compound |
| Formula Weight (FW): | 139.20 |
| Lawson Number (LN): | 25359 |




Atom/Bond Notes:

1. CIP Descriptor: S

Preparation:

PRE

Reference(s):

1. Granger; Mas, Bull.Soc.Chim.Fr., <1962>, 233, CODEN: BSCFAS

Melting Point:

| Value (MP) (Cel) | Ref. |
|---|---|
| 93.00 | 1 |

Reference(s):

1. Granger; Mas, Bull.Soc.Chim.Fr., <1962>, 233, CODEN: BSCFAS

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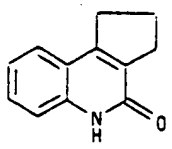
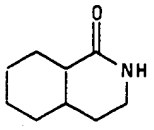
L26 ANSWER 25 OF 25 ZCAPLUS COPYRIGHT 1997 ACS
AN 1968:39866 ZCAPLUS
DN 68:39866
TI Chemistry of natural substances. VII. Furoquinoline derivatives by condensation of ethyl 2-propynyl malonate with aromatic amines
AU Reisch, Johannes
CS Westfael. Wilhelms-Univ., Muenster, Ger.
SO Arch. Pharm. Ber. Dtsch. Pharm. Ges. (1967), 300(6), 533-9
CODEN: APBDAJ
DT Journal
LA German
GI For diagram(s), see printed CA Issue.
AB Under the reaction conditions which are stated by Baker, Lappin, and Riegel (1946) for the prepn. of 3-substituted 4-hydroxyquinolin-2-one, malonic acid diarylamides and not 4-hydroxyquinolinones were obtained. By variation of the synthesis from prop-2-ynylmallonic ester and PhNH2 or MeOC5H4-NH2 resp. 5'-methylnordictamine and 5'-methylnorpseudodictaamine or 5'-methylnorfagarine (Ia) and 5'-methylnorpseudofagarine (Ib) resp. were prepd. (Method A) A mixt. of 11 g. di-Et prop-2-ynylmalonate (I) and 4.7 g. PhNH2 in 25 ml. Ph2O were refluxed 1 hr. to give 66% prop-2-ynylmalonic acid (II) dianilide (IIa), m. 217.degree. (EtOH). (Method B). To 3.8 g. freshly distd. PHNH2 in 150 ml. abs. Et2O was dropped 2 g. prop-2-ynylmalonic acid dichloride in 20 ml. Et2O with stirring and ice cooling to obtain 90% IIa. According to method A was prepd. 48% of the corresponding di-O-anisidide, m. 147.degree. (EtOH) of II; 54% of the cyclohexylmalonic acid (III) dianilide, m. 303.degree. (EtOH) and from 6.65 g. di-Et cyclohexylmalonate (IV) and 3.1 g. p-MeOC6H4NH2, 3 g. di-p-anisidide deriv., m. 289-90.degree. (EtOH) of III, beside 1 g. p-anisidide Et ester deriv., m. 158-60.degree. (aq. EtOH) of III. Heating 6 g. di-Et propylmalonate and 6 g. PhNH2 1 hr. at 190-200.degree. gave 50% propylmalonic acid dianilide (V), m. 200.degree. (EtOH). Hydrogenation of IIa in 80% MeOH at 0.degree. and 760 mm. gave V quant. A mixt. of 6.65 g. IV and 2.32 g. PhNH2 in 12.5 ml. Ph2O was heated on the descending cooler until 2.5 ml. EtOH was distd. to give 83% 3-cyclohexyl-4-hydroxy-2(1H)-quinolinone (VI), m. 238-4.degree. (EtOH). Analogously prepd. were 90% 6-methoxy deriv. m. 235-6.degree. (EtOH), of VI, and 3-propyl-4-hydroxy-2(1H)quinolinone, m. 235.degree.. A mixt. of 22 g. I and 9.3 g. PhNH2 in 50 ml. was heated on the descending cooler until 10 ml. EtOH was distd. to obtain 74% 2-methylfuro[3,2-c]quinolinone (VII), identified by ir spectroscopy. Also obtained was 16% 2-methylfuro[2,3-b]quinolin-4-one (VIII), m. 275.degree. (HCONMe2H2O). Analogously were prepd. 74% Ib m. 248-52.degree. (sublimes), and 13.5% Ia, m. 261.degree..
IT ***4514-03-8P***
(prepn. of)
RN 4514-03-8 ZCAPLUS
CN 4*H*-Cyclopenta[*c*]quinolin-4-one, 1,2,3,5-tetrahydro- (7CI, 8CI, 9CI) (CA INDEX NAME)

RN 4514-03-8 ZCAPLUS



L18 ANSWER 112 OF 155 ZCAPLUS COPYRIGHT 1997 ACS
AN 1968:505846 ZCAPLUS
DN 69:105846
TI Photochemistry of some N-hydroxy lactams
AU Di Maio, Giorgio; Tardella, Paolo Antonio
CS Univ. Roma, Rome, Italy
SO Ric. Sci. (1968), 38(3), 231-3
CODEN: RISCAZ
DT Journal
LA Italian
GI For diagram(s), see printed CA Issue.
AB N-Hydroxy lactams (I-V) were photolyzed with a high-pressure Hg lamp for 9-11 hrs. in aq. soln. to give 80-90% conversions and 11-30% yields of the dehydroxy lactams. More complex mixts. were obtained in other solvents. When the photolysis mixt. from I in EtOH was treated with 3N HCl, most of the alc. removed in vacuo, the aq. residue extd. with CHCl3, and the residue kept 30 hrs. at 100.degree. after addn. of Sn, pyrrolidine was isolated and identified as its chloroplatinate.
IT ***20597-65-3P***
(prepn. of)
RN 20597-65-3 ZCAPLUS
CN Isocarbostyril, octahydro- (6CI, 7CI, 8CI) (CA INDEX NAME)

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L9 ANSWER 5 OF 6 CAPLUS COPYRIGHT 1998 ACS
ACCESSION NUMBER: 1968:505846 CAPLUS
DOCUMENT NUMBER: 69:105846
TITLE: Photochemistry of some N-hydroxy lactams
AUTHOR(S): Di Maio, Giorgio; Tardella, Paolo Antonio
CORPORATE SOURCE: Univ. Roma, Rome, Italy
SOURCE: Ric. Sci. (1968), 38(3), 231-3
CODEN: RISCAZ
DOCUMENT TYPE: Journal
LANGUAGE: Italian
GI For diagram(s), see printed CA Issue.
AB N-Hydroxy lactams (I-V) were photolyzed with a high-pressure Hg lamp for 9-11 hrs. in aq. soln. to give 80-90% conversions and 11-30% yields of the dehydroxy lactams. More complex mixts. were obtained in other solvents. When the photolysis mixt. from I in EtOH was treated with 3N HCl, most of the alc. removed in vacuo, the aq. residue extd. with CHCl3, and the residue kept 30 hrs. at 100.degree. after addn. of Sn, pyrrolidine was isolated and identified as its chloroplatinate.
IT ***20597-65-3P***
(prepn. of)

L9 ANSWER 6 OF 6 CAPLUS COPYRIGHT 1998 ACS
ACCESSION NUMBER: 1968:39866 CAPLUS
DOCUMENT NUMBER: 68:39866
TITLE: Chemistry of natural substances. VII. Furoquinoline derivatives by condensation of ethyl 2-propynyl malonate with aromatic amines
AUTHOR(S): Reisch, Johannes
CORPORATE SOURCE: Westfael. Wilhelms-Univ., Muenster, Ger.
SOURCE: Arch. Pharm. Ber. Dtsch. Pharm. Ges. (1967), 300(6), 533-9
CODEN: APBDAJ
DOCUMENT TYPE: Journal
LANGUAGE: German
GI For diagram(s), see printed CA Issue.
AB Under the reaction conditions which are stated by Baker, Lappin, and Riegel (1946) for the prepn. of 3-substituted 4-hydroxyquinolin-2-one, malonic acid diarylamides and not 4-hydroxyquinolinones were obtained. By variation of the synthesis from prop-2-ynylmallonic ester and PhNH2 or MeOC5H4-NH2 resp. 5'-methylnordictamine and 5'-methylnorpseudodictaamine or 5'-methylnorfagarine (Ia) and 5'-methylnorpseudofagarine (Ib) resp. were prepd. (Method A) A mixt. of 11 g. di-Et prop-2-ynylmalonate (I) and 4.7 g. PhNH2 in 25 ml. Ph2O were refluxed 1 hr. to give 66% prop-2-ynylmalonic acid (II) dianilide (IIa), m. 217.degree. (EtOH). (Method B). To 3.8 g. freshly distd. PHNH2 in 150 ml. abs. Et2O was dropped 2 g. prop-2-ynylmalonic acid dichloride in 20 ml. Et2O with stirring and ice cooling to obtain 90% IIa. According to method A was prepd. 48% of the corresponding di-O-anisidide, m. 147.degree. (EtOH) of II; 54% of the cyclohexylmalonic acid (III) dianilide, m. 303.degree. (EtOH) and from 6.65 g. di-Et cyclohexylmalonate (IV) and 3.1 g. p-MeOC6H4NH2, 3 g. di-p-anisidide deriv., m. 289-90.degree. (EtOH) of III, beside 1 g. p-anisidide Et ester deriv., m. 158-60.degree. (aq. EtOH) of III. Heating 6 g. di-Et propylmalonate and 6 g. PhNH2 1 hr. at 190-200.degree. gave 50% propylmalonic acid dianilide (V), m. 200.degree. (EtOH). Hydrogenation of IIa in 80% MeOH at 0.degree. and 760 mm. gave V quant. A mixt. of 6.65 g. IV and 2.32 g. PhNH2 in 12.5 ml. Ph2O was heated on the descending cooler until 2.5 ml. EtOH was distd. to give 83% 3-cyclohexyl-4-hydroxy-2(1H)-quinolinone (VI), m. 238-4.degree. (EtOH). Analogously prepd. were 90% 6-methoxy deriv. m. 235-6.degree. (EtOH), of VI, and 3-propyl-4-hydroxy-2(1H)quinolinone, m. 235.degree.. A mixt. of 22 g. I and 9.3 g. PhNH2 in 50 ml. was heated on the descending cooler until 10 ml. EtOH was distd. to obtain 74% 2-methylfuro[3,2-c]quinolinone (VII), identified by ir spectroscopy. Also obtained was 16% 2-methylfuro[2,3-b]quinolin-4-one (VIII), m. 275.degree. (HCONMe2H2O). Analogously were prepd. 74% Ib m. 248-52.degree. (sublimes), and 13.5% Ia, m. 261.degree..
IT ***4514-03-8P***
(prepn. of)

RN 31272-83-0 ZCAPLUS

GI For diagram(s), see printed CA Issue.

AB The anthrone I was prepd. by treating the adduct from 2-benzylfuran and MeO2CC.tplbond.CCO2Me with BF3, methylating the phenolic OH of 4,2,3-PhCH2(MeO2C)2-C6H2OH, sapon. and dehydration to the anhydride, and cyclization with AlCl3. I and II were lactonized with Ac2O, converted to dibenzo[c,d,g]indoles with amines, or converted to 7H-dibenzo[d,e,h]cinnolines with hydrazines. The dibenzocinnolines showed no tautomerism. Cr2O3 oxidn. of II gave 1-carboxyanthraquinone. 2-Oxo-4,5-dihydro-2H-anthra[9,1-bc]-furan was similarly prepd. from the adduct of 2-benzylfuran with maleic anhydride.

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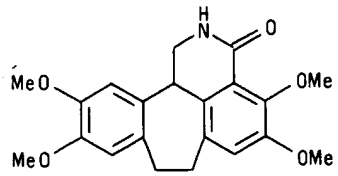
L14 ANSWER 22 OF 33 COPYRIGHT 1998 ACS

AN CA65:15320a CAOLD

IT ***7574-82-5***

RN 7574-82-5 CAOLD

CN Benzo[6,7]cyclohept[1,2,3-*de*]isoquinolin-3(2*H*)-one, 1,7,8,12b-tetrahydro-4,5,10,11-tetramethoxy- (7CI, 8CI) (CA INDEX NAME)

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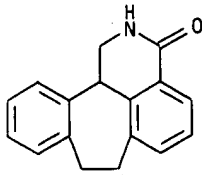
L14 ANSWER 23 OF 33 COPYRIGHT 1998 ACS

AN CA65:15319h CAOLD

IT ***7574-69-8***

RN 7574-69-8 CAOLD

CN Benzo[6,7]cyclohept[1,2,3-*de*]isoquinolin-3(2*H*)-one, 1,7,8,12b-tetrahydro- (7CI, 8CI, 9CI) (CA INDEX NAME)

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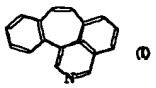
max. at 250 mμ (MeOH) and lacked the weak bands at 280 mμ, present in the corresponding ketones. II (3.7 g.) in 10 ml. $CHCl_3$ stirred at 0° with addn. of 4.0 g. $SOCl_2$ and the mixt. warmed 30 min. at 55–60°, the volatile components evapd. in vacuo, the residue taken up in a min. of alc. and the soln. made alk. with aq. $Na_2CO_3$ yielded 66.7% V ($R^1$ = Ph, $R^2$ = Me, $R^3$ = H), m. 105° ($C_6H_6$). Similarly were prepd. V ($R^1$ = Ph, $R^2$ = $R^3$ = Me) (VI), m. 141° ($C_6H_6$), and V ($R^1$ = $R^3$ = Ph, $R^2$ = Me), m. 138° ($C_6H_6$), in 78.0 and 73.5% yields, resp. Compds. in which $R^2$ = $R^1$ = H, underwent intramol. quaternization on treatment with $SOCl_2$ to give thiomorpholine derivs. (VII). III (2.7 g.) and 4.0 g. $SOCl_2$ mixed and the solvent evapd., the residue taken up in $H_2O$, the soln. made alk. and extd. with $C_6H_6$, and the chlorinated product refluxed 8 hrs. yielded 75% VII ($R^1$ = Me) (VIII), m. 224° (decompn.). Similarly was prepd. VII ($R^1$ = Me) (VIII), m. 224° (decompn.). Similarly was prepd. VII ($R^1$ = Ph) (IX), m. 230° (iso-$BuCH_2$-OH–$Et_2O$), as the hemihydrate. The uv spectra of VII ($R^1$ = H), VIII, and IX showed absorption max. at λ 249, 266 mμ (log 4.146, 4.255); 250, 271 mμ (log ε 4.111, 4.332); λ 262, 273 mμ (log ε 3.227, 3.278), whereas the nonquaternized VI, λ 254 mμ (log ε 4.161), showed no absorption at 270 mμ. EtOH (10 ml.) contg. 0.0025 mole 1-(8-quinolylthio)-2,3-butanedione and 0.0025 mole o-$(H_2N)_2C_6H_4$ in 5 ml. EtOH refluxed 5 min. gave 87.5% 2-(8-quinolylthiomethyl)-3-methylquinoxaline, m. 178° (alc.). Similarly, 1.3 g. 3-(8-quinolylthio)-2,4-pentanedione (X) and 0.5 g. $H_2NOH.HCl$ refluxed 1 hr. in 10 ml. alc. and the mixt. dild. with $H_2O$ yielded 76.9% 3,5-dimethyl-4-(8-quinolylthio)isoxazole, m. 129° (alc.). X (1.3 g.) and 1.0 g. 83% $N_2H_4.H_2O$ in 10 ml. EtOH refluxed 1 hr. with 10 ml. 50% AcOH and dild. with $H_2O$ gave 84.6% XI (R = H), m. 196° (MeOH). Similarly were produced the corresponding pyrazoles XI (R = Ph and p-$O_2NC_6H_4$), m. 132° (MeOH), m. 223° (HCONMe$_2$) in 88.2 and 89.5% yields, resp. The presence of an o-$NO_2$ group in the phenylhydrazine deriv. hindered the cyclization so that a 2nd addn. to the uncombined CO group occurred. X (1.3 g.) in 10 ml. AcOH and 1.0 g. 2,4-$(O_2N)_2C_6H_3NHNH_2$ in 20 ml. AcOH refluxed 30 min. and the filtered soln. cooled yielded 71.4% XII [R = 2,4-$(O_2N)_2C_6H_3$], m. 183° (AcOH), and 13.3% 3-(8-quinolylthio)-2,4-pentanedione bis(2,4-dinitrophenylhydrazone), m. 229° (decompn.) (HCONMe$_2$). Condensation of Et α-(8-quinolylthio)acetoacetate (XIII) with $RNHNH_2$ gave the corresponding pyrazolones (XIII, R = H, Ph, and p-$O_2NC_6H_4$), m. 260° (alc.), 208° (alc.), 220° (alc.–HCONMe$_2$), in 84.6, 82.4, and 84.2% yields, resp. The presence of an o-$NO_2$ group in the phenylhydrazine hinders the cyclization. XII (1.5 g.) and 1.0 g. 2,4-$(O_2N)_2C_6H_3NHNH_2$ refluxed in 30 ml. AcOH (concd. HCl, or 35% $HClO_4$) and the mixt. dild. with $H_2O$ gave 40–50% yields of 8-(acetonylthio)quinoline 2,4-dinitrophenylhydrazone (XIV), m. 214° (HCONMe$_2$). XII in 25 ml. alc. and 1.0 g. 2,4-$(O_2N)_2C_6H_3NHNH_2$ in 50 ml. 50% AcOH refluxed 1 hr. yielded 73.9% Et α-(8-quinolylthio)acetoacetate, 2,4-dinitrophenylhydrazone, m. 144° (HCONMe$_2$), converted (1.2 g.) by refluxing in 10 ml. AcOH (25 ml. concd. HCl, or 50 ml. 35% $HClO_4$) and quenching in $H_2O$ to yield 75–80% XIV. C. R. Addinall

**Heterocyclic compounds. I. Synthesis of aminoisoquinoline derivatives.** Teisuke Okano, Shujiro Goya, and Yoshinao Tsuda (Tohoku Univ., Sendai, Japan). *Yakugaku Zasshi* 86(7), 544–7(1966)(Japan); cf. *CA* 65, 15208b. A new method for the synthesis of 3-aminoisoquinoline derivs. was proposed where Me o-cyanomethylbenzoate (I) was treated with aq. amine under mild conditions to give an isoquinoline ring with $NH_2$ group in 3-position. Thus, 20 g. o-carboxyphenylacetonitrile is added to an ethereal soln. of 5.6 g. $CH_2N_2$, the whole kept overnight, AcOH added, evapd., and the residue distd. in vacuo to give 19 g. I, $b_2$ 135–7°, m. 48.5–49° (MeOH). Methylation of o-cyanomethylbenzoic acid also gave I. I (4 g.) and 50 ml. 28% $NH_4OH$ are heated in a sealed tube at 50–60° for 40 hrs. to give 1.8 g. 3-aminoisocarbostyril (II), m. 265° (decompn.) (MeOH); diacetate m. 177°; benzoate m. 271–2°. Similar treatment of I with $MeNH_2$ gives 2-methyl-3-aminoisocarbostyril, m. 188° (EtOH). II (1 g.) is refluxed 3 hrs. with 11 ml. $POCl_3$, an excess of $POCl_3$ removed in vacuo, the residue poured into iced $H_2O$, and the mixt. made alk. with 10% NaOH and distd. with steam to give 0.9 g. 1-chloro-2-aminoisoquinoline (III), yellow plates, m. 147–8°. Catalytic redn. of 0.2 g. III in EtOH (contg. KOH) using 10% Pd–C gives 0.1 g. 3-aminoisoquinoline, yellow needles, m. 177–8° ($C_6H_6$). Heating of 3 g. 1,3-dichloroisoquinoline in a sealed tube at 175° 6 hrs. with 50 ml. 28% $NH_4OH$ and a small amt. of $CuSO_4$ gives 2.8 g. 1-amino-3-chloroisoquinoline, m. 154–5° (EtOH) which is further subjected to catalytic redn. to give 1-aminoisoquinoline, m. 122–3° ($C_6H_6$); picrate m. 280°. Hiroshi Kataoka

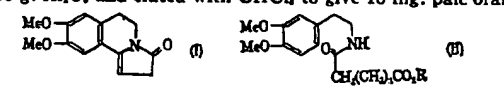
**Studies on the benzo[1,2]cyclohepta[3,4,5-d,e]isoquinoline ring system.** L. G. Humber, M. A. Davis, R. A. Thomas, R. Otson, and J. R. Watson (Ayerst Res. Labs., Montreal, Can.). *J. Heterocyclic Chem.* 3(3), 247–51(1966)(Eng). The syntheses of various oxidn. states of the novel benzo[1,2]-cyclohepta[3,4,5-*d,e*]isoquinoline (I) ring system is described. The ring system was obtained by the Schmidt rearrangement, with exclusive alkyl migration, of 1,6,7,11b-tetrahydro-2*H*-dibenz-



(I)

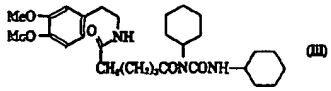
[*cd,h*]azulen-2-one and by Bischler-Napieralski reaction of suitable derivs. of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene-5-methylamine. 4,5,10,11-Tetramethoxy derivs. of the new ring system were best prepd. by a Pictet-Spengler reaction of the appropriate amine. 28 references. RCKS

**Synthesis of heterocyclic compounds. CXLI. Formation and ring closure of N-substituted imides.** Tetsuji Kametani, Ryobun Yanase, and Seiichi Takano (Tohoku Univ., Sendai, Japan). *Yakugaku Kenkyu* 37(2), 23–31(1966)(Japan); cf. *CA* 65, 5438g. *N*-(3,4-Dimethoxyphenethyl)succinimide (1 g.) is let stand for 20 days, protecting from moisture with 7.8 g. $PCl_5$ and $CHCl_3$. The resulting dark brown product is poured into iced $H_2O$, and extd. with $CHCl_3$. This is chromatographed on 30 g. $Al_2O_3$ and eluted with $CHCl_3$ to give 10 mg. pale orange

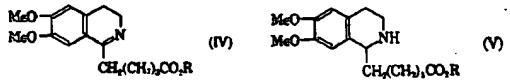


(I) (II)

granules, m. 110–11°, postulated as I. $EtO_2C(CH_2)_4CO_2H$ (5 g.) is treated with $SOCl_2$, the resulting acid chloride dissolved in 50 ml. $C_6H_6$, added to a mixt. of 5 g. homoveratrylamine, 20 ml. 10% NaOH, 50 ml. $C_6H_6$, and the whole stirred 30 min. to give 8.5 g. II (R = Et), pale yellow oil. Similarly prepd. is II (R = Bu), m. 48–9° (petroleum ether). II (R = Et) (8 g.) is stirred 3 hrs. with 50 ml. 10% NaOH, filtered, the filtrate acidified with 10% HCl, and extd. with $CHCl_3$ to give II (R = H), m. 102–3° ($C_6H_6$). To a soln. of 1 g. II (R = H) in 20 ml. $Ac_2O$ is added 3 drops pyridine and refluxed 5 hrs. to give 0.7 g. *N*-(3,4-dimethoxyphenethyl)acetamide, m. 98–9° (petroleum ether–$C_6H_6$). II (R = H) (0.5 g.) in 300 ml. $CHCl_3$ is let stand 45 hrs. with 0.4 g. dicyclohexylcarbodiimide, the mixt. filtered, the filtrate evapd., the residue dissolved in AcOEt, AcOH added, and filtered. From the filtrate is obtained *N*-[4-[*N*-(3,4-dimethoxyphenethyl)carbamoyl]valeroyl]-*N,N'*-dicyclo-



(III)

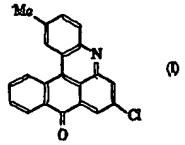


(IV) (V)

hexylurea (III), m. 118–20° ($C_6H_6$–hexane). II (R = Et) (2 g.) is refluxed with 10 g. $POCl_3$ for 2 hrs. in $C_6H_6$, kept overnight with hexane, the red oil sepd. is dissolved in 10% HCl, washed with $C_6H_6$, neutralized with 10% NaOH, and extd. with $CHCl_3$ to give 1.5 g. IV (R = Et), m. 58–9° (hexane); picrate m. 98–9°. Similarly is prepd. IV (R = Bu), m. 58–9° (petroleum ether). IV (R = Et) (1.2 g.) in a mixt. of 30 ml. EtOH and 5 ml. concd. HCl is subjected to catalytic redn. over 0.3 g. $PtO_2$ to give 1.2 g. V (R = Et), pale yellow oil, picrate m. 115–16°, which is refluxed with NaOH to give V, (R = H), red sirup. Hiroshi Kataoka

**Synthesis of heterocyclic compounds. CLIV. Novel methylation. 3. Methylation of tertiary amines such as pyridine and isoquinoline with alkyl carboxylates.** Tetsuji Kametani, Kazuo Kigasawa, Tetsutaro Hayasaka, Mineharu Hiiragi, Haruhide Ishimaru, and Setsu Asagi (School Med., Tohoku Univ., Sendai, Japan). *J. Heterocyclic Chem.* 3(2), 129–36 (1966)(Eng); cf. *CA* 63, 6911*h*; preceding abstr. The alkylation of tertiary amines, namely, 2-dimethylaminoethanol, triethylamine, pyridine, and isoquinoline with various alkyl carboxylates was investigated. This reaction afforded the corresponding quaternary ammonium salts, e.g., methylation of 2-dimethylaminoethanol with methyl salicylate. RCKS

**Direct amination of 2-methyl-7-chloroceramidonine with ammonia and sodium amide.** E. P. Fokin, R. P. Shishkina, and I. V. Pomicheva (Acad. Sci. U.S.S.R., Novosibirsk). *Khim. Geterotsikl. Soedin., Akad. Nauk Latv. SSR* 1966(3), 467–9(Russ). Amination of 1.5 millimoles 2-methyl-7-chloro-



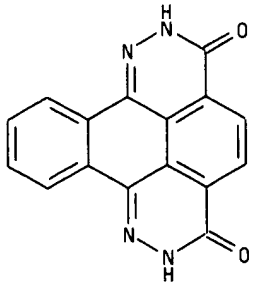
(I)

ceradonine (I) with 10 cc. 25% aq. $NH_3$ for 6–8 hrs. and heating to 170° in the presence of 0.25 g. $Cu(AcO)_2$ gave 29% 6-amino deriv.



-54-

L14 ANSWER 24 OF 33 COPYRIGHT 1998 ACS
AN CA62:9129g CAOLD
IT ***969-28-8***
RN 969-28-8 CAOLD
CN Benzo[*h*]phthalazino[7,8,1-*def*]annoline-3,6-dione, 2,7-dihydro- (8CI) (CA INDEX NAME)



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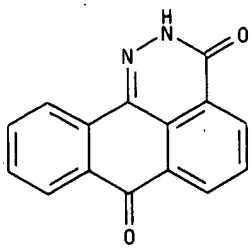
L14 ANSWER 25 OF 33 COPYRIGHT 1998 ACS
AN CA62:9129e CAOLD
IT ***731-37-3***
RN 731-37-3 CAOLD
CN 3*H*-Dibenzo[*de*,*h*]cinnoline-3,7(2*H*)-dione (7CI, 8CI, 9CI) (CA INDEX NAME)



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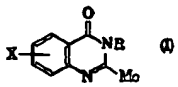
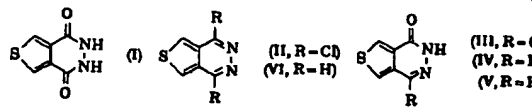
thranilic acid (4.3 g.) was refluxed with 20 ml. $Ac_2O$ 90 min. to give 2-methyl-7-chloro-4*H*-3,1-benzoxazin-4-one, which was refluxed in 100 ml. xylene with 5.4 g. *o*-toluidine to give 2-methyl-3-*o*-tolyl-7-chloro-3,4-dihydroquinazolin-4-one, m. 112–13°; HCl salt m. 240–3° (decompn.). Similarly were prepd. the following I (R, X, and m.p. given): 2-$MeC_6H_4$, 5-Cl, 159–61° *a*



(I)

(hydrate); $C_6H_{11}$, 5-Cl, 225–7° (hydrate); 2-$MeC_6H_4$, 6-Cl, 155–6°; 2-$MeC_6H_4$, 6-Cl, 213–16° (decompn.) (HCl salt); $C_6H_{11}$, 6-Cl, 183–5° (hydrate); $C_6H_{11}$, 6-Me, 183–4° (hydrate); 2-$MeC_6H_4$, 7-Cl, 112–13°; 2-$MeC_6H_4$, 7-Cl, 240-3° (HCl salt); $C_6H_{11}$, 7-Cl, 189–90°; 2-$MeC_6H_4$, 7-$NO_2$, 167–9°; $C_6H_{11}$, 7-$NO_2$, 203–5°; 2-$MeC_6H_4$, 7-$NH_2$, 201–3°; $C_6H_{11}$, 7-$NH_2$, 234–6° (hydrate); *b* 2-$MeC_6H_4$, 7-NHAc, 126–8° (hydrate); $C_6H_{11}$, 7-NHAc, 238–9° (hydrate); 2-$MeC_6H_4$, 8-Me, 131–2°. W. Lowenthal

**Synthesis of thieno[3,4-*d*]pyridazine.** Max Robba, Robert C. Moreau, and Bernard Roques (Fac. Pharm., Paris). *Compt. Rend.* 259(21), 3783–5(1964)(Fr). Treatment of I with $POCl_3$ gave pale yellow II, m. 169°, easily hydrolyzed in air or by hydroxylic solvents to form pale yellow III, m. 259°. Attempted

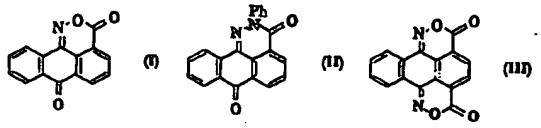


(I) (II, R = Cl) (VI, R = H) (III, R = Cl) (IV, R = Br) (V, R = H) *c*

dehalogenation of II with Al–Hg, $LiAlH_4$, Ni–H, or Pd–H led to decompn. or to III. III was also prepd. from I by careful treatment with $POCl_3$. With $POBr_3$ or $PBr_5$, I formed only IV, m. 255°. III or IV with Ni–H gave V, m. 253°. Bromination or chlorination of V failed. Treatment of 3,4-diformylthiophene with $N_2H_4$ gave VI, m. 136°. Spectral data (ir, N.M.R.) were given. J. B. Thomson

**Ion exchangers with complex-forming anchor groups. XII. Existence of ethylenediaminetriacetic acid.** G. Kuehn, E. Hoyer, and R. Hering (Karl-Marx-Univ., Leipzig, Ger.). *Z. Chem.* 4(12), 462–3(1964)(Ger); cf. *CA* 60, 1142*g*. Me 1-aziridinylacetate (9.5 g.) and 35 g. $(EtO_2CCH_2)_2NH$ was heated 25 hrs. at 80° in 45 ml. alc. with a few drop alc. HCl to give 40% the Me Et (I) ester of 2-oxopiperazine-*N*,*N*′-diacetic acid, $b_{0.001}$ 143–5°, $n_D^{25}$ 1.4813. Sapon. of I with $Ba(OH)_2$ gave the lactam of ethylenediaminetriacetic acid, 2-oxopiperazine-*N*,*N*′-diacetic acid (II), decompd. 214–15°. The 1:1 $Cu^{2+}$ complex of II with 3 moles $H_2O$ crystd. in fine light blue needles from a soln. of II and $CuNO_3$; at 120°, 2 moles $H_2O$ were lost and the other mole was lost at 135–40°. Titration curves and stability consts. of the acid and the $Ca^{2+}$, $Cu^{2+}$, and $Ni^{2+}$ complexes shows *e* the inductive effect of the oxo group makes II more acid than piperazine-*N*,*N*′-diacetic acid. Elizabeth W. Baumann

**Pyridazoanthrone and its derivatives. III. Oxazoanthrone and its connection with pyridazoanthrone.** N. S. Dokunikhin and V. Ya. Fain (Res. Inst. Org. Intermed. and Dyes, Rubezhnoe). *Zh. Obshch. Khim.* 34(11), 3769–71(1964)(Russ); cf. *CA* 62, 4027*e*. Oxazoanthrone (I) (cf. Ullmann and van der Schalk, *Ann.* 388, 199(1912)) heated in AcOH with $N_2H_4$ 6 hrs. gave 30.1% pyridazoanthrone, m. 425–6°. Similarly, $PhNHNH_2$ gave *N*-phenylpyridazoanthrone (II), m. 290.3–1.0°. I heated with Br in AcOH in a sealed tube 2.5 hrs. at 150° gave *f* after an aq. treatment anthraquinone-1-carboxylic acid, m. 292–3°. I refluxed with 98% $HNO_3$ gave the same acid in 88% yield. 4-Aminoanthraquinone-1-carboxylic acid refluxed 0.5 hr. with aq.

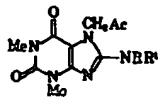


(I) (II) (III)

KOAc and $HONH_2.H_2SO_4$, then with aq. $NH_4OH$, gave on acidification 78.3% 4-aminooxazoanthrone, decompd. 291°. Similarly was prepd. 83.3% 5-aminooxazoanthrone, decompd. 283°. Anthraquinone-1,4-dicarboxylic acid refluxed as above with $HONH_2.H_2SO_4$ gave anthra-1,9(*N*),10(*N*),4-dioxazone (III), decompd. 318–19°. Spectral data (uv) on these products were reported. G. M. Kosolapoff *g*

**Synthesis in the theophylline series. X. Syntheses of xanthine amino acids.** Josef Klosa. *J. Prakt. Chem.* 26(1–2), 48–53(1964)(Ger); cf. *CA* 55, 5511*d*. 7-Acetonyl-8-chlorotheophylline (I) or the Br analog was converted with amino acids in the presence of alkali nto the corresponding 7-acetonyl-8-thiophyllinylamino acids. I (27 g.) in 60 cc. $H_2O$ treated with stirring with 10 g. $H_2NCH_2CO_2H$ and adjusted with 2*N* NaOH to pH 8–9, refluxed with stirring while being maintained at pH 7.5–8.5 by the dropwise addn. of 2*N* NaOH, and refluxed an addnl. hr. yielded 32 g. II (R = $NHCH_2CO_2H$, $R^1$ = H) (III), m. 294–6° *h*

(decompn.) with browning from 260°. III dissolved in an equiv. amt. aq. 50% NaOH and dild. with EtOH yielded the Na salt of III, m. >330° (decompn.). III (6.2 g.) and 4 g. L-ephedrine (IV) refluxed in MeOH to soln. and cooled gave 9 g. III-IV salt, m.

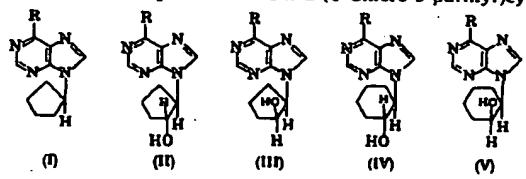


(II)

218–20°. Similarly were prepd. the following II ($R^1$ = H) (R, m.p., and % yield given): $CH_3CH_2CO_2H$, 270–2°, 85; $CHMeCO_2H$, 233–5°, 70; $PhCHCO_2H$, 145–7°, 60; $PhCH_2CHCO_2H$, 230–2°, 70; *p*-$HOC_6H_4CH_2CHCO_2H$, 258–60°, 60; $EtCHCO_2H$, 215–17°, 60; $MeCHCH_2CO_2H$, 254–6°, 55; $(CH_2)_2CO_2H$, 238–8°, 45; $(CH_2)_3CO_2H$, 226–8°, 65; iso-$PrCHCO_2H$, 204–6°, 40; $EtMeCCO_2H$, 223–5°, 45; iso-$BuCHCO_2H$, 128–8°, 60; $HO_2C$-$CHCH_2CO_2H$, 228–30° (aq. MeOH), 85; $HO_2CCHCH_2CONH_2$, 258–60° (85% iso-PrOH), 85; $HO_2CCH_2CH_2CHCO_2H$, 102–4° (aq. MeOH), 80; $H_2NOCCH_2CH_2CHCO_2H$, 263–5° (90% iso-PrOH), 80; $MeSCH_2CH_2CHCO_2H$, 194–6°, 75. II did not exhibit any pharmacol. activity; their $L.D._{50}$ values are above 3 g. orally. The III-IV salt is not only more toxic than III, but it exhibited also a 30% increase of the hypotensive activity of IV with considerable prolongation of the effect. **XI. Synthesis of 7-acetonyltheophyllines.** *Ibid.* (3–4), 155–8. I or the Br analog with dialkylaminoalkylamines yielded the corresponding II under mild conditions. I (27 g.) and 11.6 g. $Et_2NCH_2CH_2NH_2$ in 100 cc. iso-PrOH refluxed 5 hrs. yielded 25 g. II (R = H, $R^1$ = $CH_2$-$CH_2NEt_2$) (V), m. 143–5° (repptd. from MePh with petr. ether); V. HCl m. 288–90°; V. MeBr m. 297–9°. Similarly were prepd. the following II (R, $R^1$, and m.ps. of base and HCl salt given): H, $Et_2N(CH_2)_3$, 118–20°, 260–2° (methobromide m. 238–40°); H, $Me_2N(CH_2)_3$, 125–7°, 240–2° (methobromide m. 225–7°); Me, $Et_2NCH_2CH_2$, 98, — (hygroscopic); Me, $Me_2NCH_2CH_2$, 114–16°, 254–6°; H, 2-piperidinoethyl, 158–60°, —; H, 2-morpholinoethyl, 198–200°, 266–8°; H, 3-cyclohexylaminopropyl, 120–2°, 325–7°. Similarly was prepd. II [(RR$^1$ =) 4-methylpiperazino)], m. 135–7°; HCl salt m. 272–4°. II did not reach *d* the pharmacol. activity of theophylline, caffeine, or 7-acetonyltheophylline. F. W. Hoffmann

**Some purine azides.** N. B. Smirnova and I. Ya. Postovskii (S. M. Kirov Polytech. Inst., Sverdlovsk). *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva* 9(6), 711–12(1964)(Russ). 2,6-Dichloropurine and $NaN_3$ refluxed 5 min. in aq. EtOH gave 75% 2,6-diazidopurine (I), decompd. 190–200°; similarly was prepd. 2,6,8-triazidopurine, decompd. 180–90°. I refluxed 1 hr. in aq. piperidine gave 82% 6-(*N*-piperidinyl)-2-azidopurine, decompd. 215–16°. Similarly were prepd. 6-morpholino-2-azidopurine, decompd. about 260°, 6-(*N*-piperidinyl)-2,8-diazidopurine, decompd. 190–200°, and 6-morpholino-2,8-diazidopurine, decompd. 190–200°. Uv spectra of the products were reported. G. M. Kosolapoff

**Enzyme inhibitors. I. Inhibition of adenosine deaminase by isosteric nucleosides.** Howard J. Schaeffer, S. Marathe, and Vitauts Alks (State Univ. of New York, Buffalo). *J. Pharm. Sci.* 53(11), 1368–70(1964)(Eng). A study was made of the important sites for adenosine binding to the enzyme. A series of known isosteric nucleosides were prepd. by published methods, which were purines contg. at the 9-position a cyclopentyl or a cyclohexyl ring substituted in such a manner that they simulated sterically the sugar moiety of a nucleoside. The compds. fell into 5 types (i.e. I-V) depending upon the ring substituted at the 9-position. Attached to the 6-position of the purine nucleus was an $NH_2$, SH, $NHNH_2$, H, or Cl group. The $NH_2$ group was the only one of the 6-position groups which produced inhibition. For effective inhibition it was also necessary to have the ring substitution at the 9-position. *trans*-2-(6-Chloro-9-purinyl)cyclo-



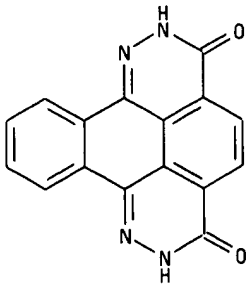
(I) (II) (III) (IV) (V)

pentanol (0.288 g.) in 10 ml. EtOH was treated with 10 ml. 40% aq. $MeNH_2$ and the mixt. refluxed 3 hrs. to give 59.3% the 6-methylamino analog, m. 194–5°. **II. Synthesis of *trans*-3-(6-substituted-9-purinyl)cyclohexanols as adenosine deaminase inhibitors.** Howard J. Schaeffer, K. K. Kaistha, and S. K. Chakraborti. *Ibid.* 1371–4. 5-Amino-4,6-dichloropyrimidine (5.05 g.), 3.58 g. *trans*-3-aminocyclohexanol (Ia), and 3.1 g. $Et_3N$ in 46 ml. BuOH refluxed 6.5 hrs. gave 77% *trans*-3-(5-amino-6-chloro-4-pyrimidinylamino)cyclohexanol (I), m. 229–31°. I (2 g.) and 25 ml. $HC(OEt)_3$ was refluxed 48 hrs., evapd., and the residue kept 20 hrs. at 0° with 25 ml. 20% $NH_3$ in MeOH to give 20% 6-chloro-9-(3-cyclohexenyl)purine, m. 162°, and 35%



-55-

L14 ANSWER 26 OF 33 COPYRIGHT 1998 ACS
AN CA61:9494a CAOLD
IT ***969-28-8*** ***97594-69-9*** ***98000-26-1***
RN 969-28-8 CAOLD
CN Benzo[*h*]phthalazino[7,8,1-*def*]annoline-3,6-dione, 2,7-dihydro- (8CI) (CA INDEX NAME)



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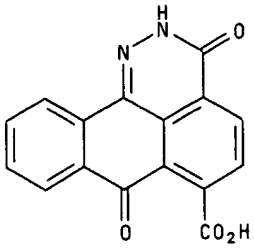

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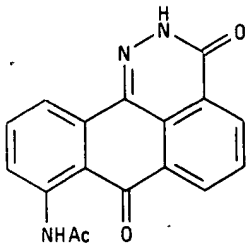
CN 3*H*-Dibenzo[*de,h*]cinnoline-3,7(2*H*)-dione, 8-acetamido- (7CI) (CA INDEX NAME)



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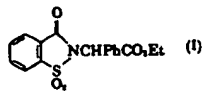
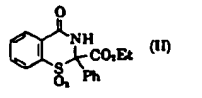
3-methyl-2-phenyl-2*H*-1,3-benzothiazin-4(3*H*)-one, which with 30% $H_2O_2$ gave IV. Alk. treatment of II resulted in destruction

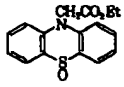

(I)


(II)

of the 1,3-benzothiazine system as shown by the rapid liberation of BzH and the isolation of *o*-$HO_2CC_6H_4SO_2H$. Evidently initial sapon. and decarboxylation occurred to give 2-phenyl-2*H*-1,3-benzothiazin-4(3*H*)-one 1,1-dioxide (V), unstable to alkali. Treatment of I with NaH in $HCONMe_2$ at 20° gave V.

C. R. Addinall

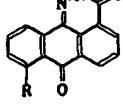
**Preparation of some derivatives of 10-carboxymethylphenothiazine.** D. Simov and St. Fakirov. *Godishnik Sofiiskiya Univ. Khim. Fak.* 56, 111–21(1961/62). Carbethoxymethylphenothiazine (I) (3 g.) suspended in 40 ml. glacial AcOH was treated with 1.2 g. $NaNO_2$ 3 hrs. with stirring and cooling, the mixt. filtered, and the filtrate treated with 200 ml. $H_2O$ to yield 84% 10-carbethoxymethylphenothiazine 5-oxide (II), m. 203–4°

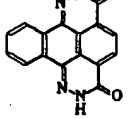

(II)

(EtOAc). II was also prepd. in 80% yield by oxidizing I with $H_2O_2$ in EtOH. Heating a soln. of 1.5 g. II in 15 ml. 3% alc. KOH 4–5 min. on a water bath and neutralizing with alc. HCl gave 88% yield of 10-carboxymethylphenothiazine 5-oxide, m. 239–40° (AcOH). A soln. of 3 g. I in 15 ml. dioxane was treated with 8 ml. 30% aq. $H_2O_2$ during 2 hrs. The mixt. was then heated another 2 hrs. and cooled to yield 93% 10-carbethoxymethylphenothiazine 5-dioxide (III), m. 163–4° (EtOAc); III hydrolyzed as above gave the corresponding acid, m. 262–3.5°. To a soln. of 2 g. I in 20 ml. glacial AcOH was added 1 ml. fuming $HNO_3$ and 2 hrs. later another 1 ml. The mixt. was stored overnight and stirred into 100 ml. $H_2O$; the resulting ppt. was recrystd. from EtOH to yield 80% nitro deriv. of II, m. 171–2°, which upon hydrolysis gave the acid, m. 222–3°. The nitro deriv. of III was prepd. by nitration of III in the cold or by nitration of II under reflux followed by oxidn. with aq. $H_2O_2$. Treatment of I with 8 ml. fuming $HNO_3$ as above yielded 92% dinitro deriv. of II, m. 220–2°, which upon oxidn. with aq. $H_2O_2$ gave the dinitro deriv. of III, m. 239–40°. G. H. Meguerian

**Action of nitric acid on polybromophenothiazines.** Cornel Bodea, V. Farcasan, and I. Oprean (Chem. Inst., Cluj, Romania). *Zh. Obshch. Khim.* 34(7), 2369–71(1964); cf. *CA* 55, 550*b*. Nitration of polybromophenothiazine-5,5-dioxides in fuming $HNO_3$ with ice cooling, followed by 12 hrs. at room temp., gave the following products: 1,9-dibromo-3,7-dinitrophenothiazine 5,5-dioxide, m. 305°, formed from 1,3,7,9-tetrabromophenothiazine dioxide or 1,3,7,9-tetrabromophenothiazine; 1,3,7,9-tetranitrophenothiazine 5,5-dioxide, m. 344–5°, formed from 3,7-dibromophenothiazine 5,5-dioxide, or 3,7-dibromophenothiazine; 1-bromo-3,7,9-trinitrophenothiazine 5,5-dioxide, m. 311–12°, formed from 1,3,7-tribromophenothiazine 5,5-dioxide or 1,3,7-tribromophenothiazine; 1-nitro-3,7-dibromophenothiazine 5,5-dioxide, m. 297–8°, formed from 3,7-dibromophenothiazine 5,5-dioxide by heating with fuming $HNO_3$ in AcOH 2 min. at reflux. G. M. Koslapoff

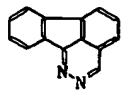
**Pyridazoneanthrone and its derivatives. I.** N. S. Dokunikhin and V. Ya. Fain. *Zh. Obshch. Khim.* 34(7), 2372–4(1964). Refluxing anthraquinone-1-carboxylic acid in aq. NaOAc in the presence of $N_2H_4.H_2SO_4$ 7 hrs. gave 93% pyridazoneanthrone (I, R = H) (II), m. 426–7°; simple heating of the acid with $N_2H_4.H_2O$ 3 hrs. gave a 92.5% yield. Similar reaction of 4-aminoanthraquinone-1-carboxylic acid gave 85.7% 4-aminopyridazoneanthrone, decompd. 351.5–2.8°, also formed in 74.6% yield from 4-nitroanthraquinone-1-carboxylic acid refluxed 1 hr. with $PCl_5$ in $C_6H_6$, then treated in the cold with $N_2H_4.H_2O$ 1 hr., followed by refluxing with dil. $NH_4OH$; the use of $N_2H_4.H_2SO_4$ gave an 82.7% yield. II nitrated in concd. $H_2SO_4$ with 98% $HNO_3$ at 0° 1 hr. gave I (R = $NO_2$), decompd. 291.2–3°, which with aq. $Na_2S$ 1.5 hrs. at reflux gave 89% I (R = $NH_2$), decompd. 372–3°, also formed in 91.5% yield from 5-aminoanthraquinone-1-carboxylic acid, via the route used above for prepn. of II. I (R = $NH_2$) was also formed by treatment of 5-nitroanthraquinone-1-carboxylic acid with $PCl_5$ and $N_2H_4$, as shown above, the


(I)


(IV)

yield being 70.2%. The amine heated with $Ac_2O$ 0.5 hr. gave I (R = AcNH), decompd. 370–1°. Anthraquinone-1,4-dicarboxylic acid (III) heated successively with $PCl_5$, then $N_2H_4.H_2O$ gave 92.5% anthra-1,4-dipyridazone (IV), decompd. about 500°. III in hot aq. NaOAc was treated with $N_2H_4.H_2SO_4$ and refluxed 3 hrs. to yield 4% insol. IV, and 93.6% pyridazoneanthrone-4-carboxylic acid, decompd. 333.5–4.8°. G. M. Kosolapoff

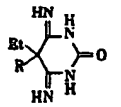
**Transformation of 3-hydrazinopyridazino[4,5,6-*m*,*l*]fluorene.** N. S. Dokunikhin and S. A. Mikhalenko. *Zh. Obshch. Khim.* 34(7), 2473–4(1964). 3-Chloropyridazino[4,5,6-*m*,*l*]fluorene and $N_2H_4.H_2O$ gave the 3-hydrazino analog, isolated as the hydrate (I), which with HgO in alc. NaOH gave 80% pyridazino[4,5,6-*m*,*l*]fluorene (II), m. 123.6–25°; in the absence of HgO the yield was 54%. I, decompd. 255.6–56°, and 2 moles aq. $CuSO_4$


(II)

gave 85% 1-cyanofluorenone, m. 180–80.5°, also formed in 10% yield in alc. NaOH. Sapon. with alc. alkali gave fluorenone-1-carboxylic acid. Similarly, 3-hydrazino-9-methylpyridazino-[4,5,6-*m*,*l*]fluorene hydrate, m. 277.5–8.6°, gave 60% 1-cyano-7-methylfluorenone, m. 209.1–10°. I was unchanged by oxidizing agents such as $Na_2AsO_4$. II picrate decompd. 221–2°.

G. M. Kosolapoff

**Synthetic organic chemistry using liquid ammonia alkali hydroxide. XIX. New barbituric acid synthesis in liquid ammonia-alkali hydroxide. 8. Synthesis of ethylalkyldiiminobarbituric acid by the condensation of ethylalkylmalononitrile with urea.** Kotaro Shimo and Toshio Kawasaki (Natl. Defence Acad., Yokosuka, Japan). *Kogyo Kagaku Zasshi* 67(4), 574–6 (1964); cf. *CA* 58, 9072*b*. A reaction between 0.05 mole $EtHC(CN)_2$ (I) and 0.055 mole $PhCH_2Cl$ in 110 cc. liquid $NH_3$ at room temp. 1.5 hrs. gave 78% $EtPhCH_2C(CN)_2$, m. 61–1.5°, after evapn. of $NH_3$, extn. with alc., followed by evapn. of alc. and washing with water. Similarly were prepd. following $REtC(CN)_2$ (II) (R, b.p., and % yield given): $CH_2$:$CHCH_2$, 94–5°/21, 68; iso-$C_4H_{11}$, 115–16°/20, 47; Pr, 95–6°/20, 57,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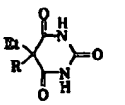

(IV)

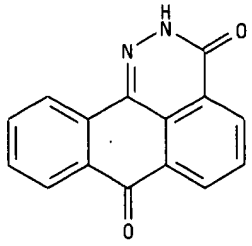
from the reactions of I and the corresponding alkyl bromides. A reaction of 0.015 mole II (R = $PhCH_2$) with 0.015 mole urea in the presence of 0.03 mole $NaNH_2$ (or NaOH) in 70 cc. liquid $NH_3$ at room temp. 3 hrs. gave 61% III (R = $PhCH_2$), m. 285–6° (decompn.), after evapn. of $NH_3$, extn. with alc. and subsequent neutralization with AcOH. Also were prepd. following III (R, m.p., and % yield given): iso-Am, 268.5–69° (decompn.), 52; $CH_2$:$CHCH_2$, 277.5–78° (decompn.), 57; Pr, 273.5–74° (decompn.), 47, while II (R = H and Ph) did not give the corresponding derivs. III readily gave the corresponding IV when heated with dil. HCl 2 hrs. (R and m.p. given): $PhCH_2$, 208–7.5°; iso-Am, 154.5–55°; allyl, 157–7.5°; and Pr, 146–6.5°. T. Takiguchi

**Cinnolines. I. *N*-oxidation of 4-chlorocinnoline and 4-methoxycinnoline.** Ikuo Suzuki and Toshiaki Nakashima (Natl. Inst. Hyg. Sci. Tokyo). *Chem. Pharm. Bull.* (Tokyo) 12(5), 619–23 (1964). 4-Chlorocinnoline (I) 1-oxide, 4-chlorocinnoline 2-oxide (II), 4-methoxycinnoline 1-oxide (III) 4-methoxycinnoline 2-oxide (IV), 4-ethoxycinnoline 2-oxide (V), 4-hydroxycinnoline 1-oxide (VI), and 4-hydroxycinnoline 2-oxide (VII) were prepd. Treating VII with MeI yielded IV and VI treated with MeI yielded III and 1-methoxy-4(1*H*)-cinnoline (VIII). II, m. 150–1°, was obtained in 43% yield by treating 7.7 g. chlorocinnoline with phthalic monoperacid in 250 ml. $Et_2O$ 2 weeks, evapg. $Et_2O$, extg. the residue with $CHCl_3$, washing with $NaHCO_3$, and recrystg. from $C_6H_6$. I, m. 94–4.5°, was obtained in 28% yield from $C_6H_6$, passed through a $Al_2O_3$ column, and recrystd from $Et_2O$. I gave cinnoline 1-oxide after hydrogenation. I was also obtained by treating 4-nitrocinnoline 1-oxide with AcCl. V, m. 190–1°, was obtained in 85% yield by treating a mixt. of 0.2 g. II with NaOEt in EtOH contg. 29 mg. Na on a steambath, evapg. EtOH, extg. with $CHCl_3$, passing the mixt. through a $Al_2O_3$ column, and recrystg. from $C_6H_6$. II yielded cinnoline 2-oxide, m. 122–3°, in 31% yield upon hydrogenation. After evapn. of the solvent from the hydrogenation, V, m. 190–1°, 19% yield was isolated. III, m. 100–5°, 77% yield was obtained by heating a mixt. of 0.2 g. I, 2 ml. MeOH, and NaOMe on a steambath 30 min., the MeOH evapd., and the residue extd. with $CHCl_3$, passed through a $Al_2O_3$ column, and recrystd. from iso-$Pr_2O$. A mixt. of 0.2 g. 4-nitrocinnoline 1-oxide with 2 ml. MeOH contg. some NaOMe was heated on a steambath 30 min. to yield III in 65% yield. IV, m. 176–7°, 92% yield was obtained from II by the same method of prepn. as for III. IV was also ob-



-56-

L14 ANSWER 28 OF 33 COPYRIGHT 1998 ACS
AN CA61:9493f CAOLD
IT ***731-37-3***
RN 731-37-3 CAOLD
CN 3*H*-Dibenzo[*de*,*h*]cinnoline-3,7(2*H*)-dione (7CI, 8CI, 9CI) (CA INDEX NAME)



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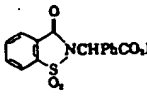
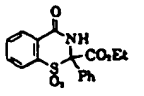
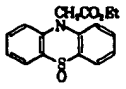
3-methyl-2-phenyl-2*H*-1,3-benzothiazin-4(3*H*)-one, which with 30% $H_2O_2$ gave IV. Alk. treatment of II resulted in destruction


(I)


(II)

of the 1,3-benzothiazine system as shown by the rapid liberation of BzH and the isolation of *o*-$HO_2CC_6H_3SO_2H$. Evidently initial sapon. and decarboxylation occurred to give 2-phenyl-2*H*-1,3-benzothiazin-4(3*H*)-one 1,1-dioxide (V), unstable to alkali. Treatment of I with NaH in $HCONMe_2$ at 20° gave V.
C. R. Addinall

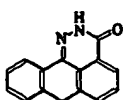
**Preparation of some derivatives of 10-carboxymethylphenothiazine.** D. Simov and St. Fakirov. *Godishnik Sofiiskiya Univ. Khim. Fak.* 56, 111–21(1961/62). Carbethoxymethylphenothiazine (I) (3 g.) suspended in 40 ml. glacial AcOH was treated with 1.2 g. $NaNO_2$ 3 hrs. with stirring and cooling, the mixt. filtered, and the filtrate treated with 200 ml. $H_2O$ to yield 84% 10-carbethoxymethylphenothiazine 5-oxide (II), m. 203–4°

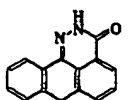

(II)

(EtOAc). II was also prepd. in 80% yield by oxidizing I with $H_2O_2$ in EtOH. Heating a soln. of 1.5 g. II in 15 ml. 3% alc. KOH 4–5 min. on a water bath and neutralizing with alc. HCl gave 88% yield of 10-carboxymethylphenothiazine 5-oxide, m. 239–40° (AcOH). A soln. of 3 g. I in 15 ml. dioxane was treated with 8 ml. 30% aq. $H_2O_2$ during 2 hrs. The mixt. was then heated another 2 hrs. and cooled to yield 93% 10-carbethoxymethylphenothiazine 5-dioxide (III), m. 163–4° (EtOAc); III hydrolyzed as above gave the corresponding acid, m. 262–3.5°. To a soln. of 2 g. I in 20 ml. glacial AcOH was added 1 ml. fuming $HNO_3$ and 2 hrs. later another 1 ml. The mixt. was stored overnight and stirred into 100 ml. $H_2O$; the resulting ppt. was recrystd. from EtOH to yield 90% nitro deriv. of II, m. 171–2°, which upon hydrolysis gave the acid, m. 222–3°. The nitro deriv. of III was prepd. by nitration of III in the cold or by nitration of II under reflux followed by oxidn. with aq. $H_2O_2$. Treatment of I with 8 ml. fuming $HNO_3$ as above yielded 92% dinitro deriv. of II, m. 220–2°, which upon oxidn. with aq. $H_2O_2$ gave the dinitro deriv. of III, m. 239–40°. G. H. Meguerian

**Action of nitric acid on polybromophenothiazines.** Cornel Bodea, V. Farcasan, and I. Oprean (Chem. Inst., Cluj, Romania). *Zh. Obshch. Khim.* 34(7), 2369–71(1964); cf. *CA* 55, 550*b*. Nitration of polybromophenothiazine-5,5-dioxides in fuming $HNO_3$ with ice cooling, followed by 12 hrs. at room temp., gave the following products: 1,9-dibromo-3,7-dinitrophenothiazine 5,5-dioxide, m. 305°, formed from 1,3,7,9-tetrabromophenothiazine dioxide or 1,3,7,9-tetrabromophenothiazine; 1,3,7,9-tetranitrophenothiazine 5,5-dioxide, m. 344–5°, formed from 3,7-dibromophenothiazine 5,5-dioxide, or 3,7-dibromophenothiazine; 1-bromo-3,7,9-trinitrophenothiazine 5,5-dioxide, m. 311–12°, formed from 1,3,7-tribromophenothiazine 5,5-dioxide or 1,3,7-tribromophenothiazine; 1-nitro-3,7-dibromophenothiazine 5,5-dioxide, m. 297–8°, formed from 3,7-dibromophenothiazine 5,5-dioxide by heating with fuming $HNO_3$ in AcOH 2 min. at reflux. G. M. Koslapoff

**Pyridazoneanthrone and its derivatives.** I. N. S. Dokunikhin and V. Ya. Fain. *Zh. Obshch. Khim.* 34(7), 2372–4(1964). Refluxing anthraquinone-1-carboxylic acid in aq. NaOAc in the presence of $N_2H_4.H_2SO_4$ 7 hrs. gave 93% pyridazoneanthrone (I, R = H) (II), m. 426–7°; simple heating of the acid with $N_2H_4.H_2O$ 3 hrs. gave a 92.5% yield. Similar reaction of 4-aminoanthraquinone-1-carboxylic acid gave 85.7% 4-aminopyridazoneanthrone, decompd. 351.5–2.8°, also formed in 74.6% yield from 4-nitroanthraquinone-1-carboxylic acid refluxed 1 hr. with $PCl_5$ in $C_6H_6$, then treated in the cold with $N_2H_4.H_2O$ 1 hr., followed by refluxing with dil. $NH_4OH$; the use of $N_2H_4.H_2SO_4$ gave an 82.7% yield. II nitrated in concd. $H_2SO_4$ with 98% $HNO_3$ at 0° 1 hr. gave I (R = $NO_2$), decompd. 291.2–3°, which with aq. $Na_2S$ 1.5 hrs. at reflux gave 89% I (R = $NH_2$), decompd. 372–3°, also formed in 91.5% yield from 5-aminoanthraquinone-1-carboxylic acid, via the route used above for prepn. of II. I (R = $NH_2$) was also formed by treatment of 5-nitroanthraquinone-1-carboxylic acid with $PCl_5$ and $N_2H_4$, as shown above, the yield being 70.2%. The amine heated with $Ac_2O$ 0.5 hr. gave I (R = AcNH), decompd. 370–1°. Anthraquinone-1,4-dicarboxylic acid (III) heated successively with $PCl_5$, then $N_2H_4.H_2O$ gave 92.5% anthra-1,4-dipyridazone (IV), decompd. about 500°. III in hot aq. NaOAc was treated with $N_2H_4.H_2SO_4$ and refluxed 3 hrs. to yield 4% insol. IV, and 93.6% pyridazoneanthrone-4-carboxylic acid, decompd. 333.5–4.8°. G. M. Kosolapoff


(I)


(IV)

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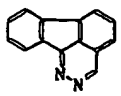
(II)

gave 85% 1-cyanofluorenone, m. 180–80.5°, also formed in 10% yield in alc. NaOH. Sapon. with alc. alkali gave fluorenone-1-carboxylic acid. Similarly, 3-hydrazino-9-methylpyridazino-[4,5,6-*m*,*l*]fluorene hydrate, m. 277.5–8.6°, gave 60% 1-cyano-7-methylfluorenone, m. 209.1–10°. I was unchanged by oxidizing agents such as $Na_3AsO_4$. II picrate decompd. 221–2°.
G. M. Kosolapoff

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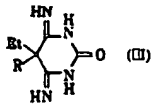
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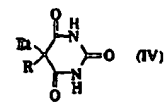
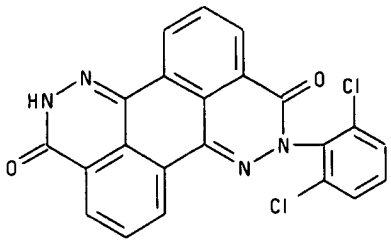

(IV)

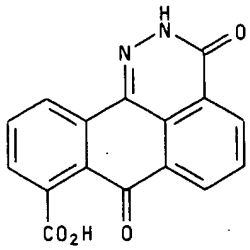
from the reactions of I and the corresponding alkyl bromides. A reaction of 0.015 mole II (R = $PhCH_2$) with 0.015 mole urea in the presence of 0.03 mole $NaNH_2$ (or NaOH) in 70 cc. liquid $NH_3$ at room temp. 3 hrs. gave 61% III (R = $PhCH_2$), m. 285–6° (decompn.), after evapn. of $NH_3$, extn. with alc. and subsequent neutralization with AcOH. Also were prepd. following III (R, m.p., and % yield given): iso-Am, 268.5–69° (decompn.), 52; $CH_2{:}CHCH_2$, 277.5–78° (decompn.), 57; Pr, 273.5–74° (decompn.), 47, while II (R = H and Ph) did not give the corresponding derivs. III readily gave the corresponding IV when heated with dil. HCl 2 hrs. (R and m.p. given): $PhCH_2$, 208–7.5°; iso-Am, 154.5–55°; allyl, 157–7.5°; and Pr, 146–6.5°. T. Takiguchi

**Cinnolines. I. *N*-oxidation of 4-chlorocinnoline and 4-methoxycinnoline.** Ikuo Suzuki and Toshiaki Nakashima (Natl. Inst. Hyg. Sci. Tokyo). *Chem. Pharm. Bull.* (Tokyo) 12(5), 619–23 (1964). 4-Chlorocinnoline (I) 1-oxide, 4-chlorocinnoline 2-oxide (II), 4-methoxycinnoline 1-oxide (III) 4-methoxycinnoline 2-oxide (IV), 4-ethoxycinnoline 2-oxide (V), 4-hydroxycinnoline 1-oxide (VI), and 4-hydroxycinnoline 2-oxide (VII) were prepd. Treating VII with MeI yielded IV and VI treated with MeI yielded III and 1-methoxy-4(1*H*)-cinnoline (VIII). II, m. 150–1°, was obtained in 43% yield by treating 7.7 g. chlorocinnoline with phthalic monoperacid in 250 ml. $Et_2O$ 2 weeks, evapg. $Et_2O$, extg. the residue with $CHCl_3$, washing with $NaHCO_3$, and recrystg. from $C_6H_6$. I, m. 94–4.5°, was obtained in 28% yield from $C_6H_6$, passed through a $Al_2O_3$ column, and recrystd. from $Et_2O$. I gave cinnoline 1-oxide after hydrogenation, I was also obtained by treating 4-nitrocinnoline 1-oxide with AcCl. V, m. 190–1°, was obtained in 85% yield by treating a mixt. of 0.2 g. II with NaOEt in EtOH contg. 29 mg. Na on a steambath, evapg. EtOH, extg. with $CHCl_3$, passing the mixt. through a $Al_2O_3$ column, and recrystg. from $C_6H_6$. II yielded cinnoline 2-oxide, m. 122–3°, in 31% yield upon hydrogenation. After evapn. of the solvent from the hydrogenation, V, m. 190–1°, 19% yield was isolated. III, m. 100–5°, 77% yield was obtained by heating a mixt. of 0.2 g. I, 2 ml. MeOH, and NaOMe on a steambath 30 min., the MeOH evapd., and the residue extd. with $CHCl_3$, passed through a $Al_2O_3$ column, and recrystd. from iso-$Pr_2O$. A mixt. of 0.2 g. 4-nitrocinnoline 1-oxide with 2 ml. MeOH contg. some NaOMe was heated on a steambath 30 min. to yield III in 65% yield. IV, m. 176–7°, 92% yield was obtained from II by the same method of prepn. as for III. IV was also ob-

L14 ANSWER 29 OF 33 COPYRIGHT 1998 ACS
AN CA55:12868c CAOLD
DT Patent
IT ***114305-05-4*** ***132647-76-8***
RN 114305-05-4 CAOLD
CN Benzo[1,2,3-*de*:4,5,6-*d'e'*]diphthalazine-3,9-dione, 2-(2,6-dichlorophenyl)-2,8-dihydro- (6CI) (CA INDEX NAME)




RN 132647-76-8 CAOLD
CN 7*H*-Dibenzo[*de*,*h*]cinnoline-8-carboxylic acid, 2,3-dihydro-3,7-dioxo- (6CI) (CA INDEX NAME)

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results in an extremely thick viscous mass from which filaments can be drawn which when stretched possess considerable tensile strength. On heating to 120°, the filaments can be tempered and the formation of crystallites observed. The cryst. polyester melts at 230–1° and has $H_2O$-absorption capacity. P. V. Bonsignore

Polyglycol ether derivatives as leveling agents. C I B A Ltd. (by Otto Albrecht). Ger. 1,060,595, July 2, 1959 (Cl. 39*c*). Ethylene oxide is treated with bases having the general formula $H_2N[R(NHR)_{m-1}HN]_{p-1}H$, in which R is alkylene, *m* and *p* are 1 or 2 each, and in which at least 1 H atom and at least 2 aliphatic or cycloaliphatic (together contg. at least 20 C atoms) groups are bound to N atoms, so that at least 1 hydrocarbon group and at most 1 acyl group is derived from a fatty acid or cycloaliphatic monocarboxylic acid. Di-*n*-decylamine (I), di-*n*-hexadecylamine (II), and the reaction products of *n*-alkylpropylenediamines with high-mol.-wt. fatty acids are suitable raw materials which are treated with ethylene oxide until the product contains 40–100 $CH_2CH_2O$ groups. For example, 30 parts of a mixt. of secondary amines with unbranched alkyl groups contg. dioctylamine 8, I 9, didodecylamine 48, ditetradecylamine 18, II 8, and dioctadecylamine 10% is heated in N stream at 120°. After the addn. of 0.3 part metallic Na, 212 parts ethylene oxide is passed in. The polyglycol deriv. obtained forms a wax, sol. in $H_2O$. It is suitable as a leveling agent for acid wool dyes. R. Degenkolbe

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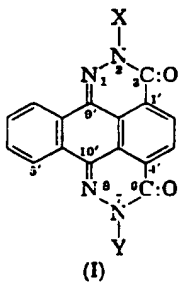
Anthradipyridazones and their use in polymeric materials as optical bleaching agents. Imperial Chemical Industries Ltd. (by Francis Irving, Charles H. Reece, Neil Munro, and Robert H. Wilson). Brit. 838,994, June 22, 1960. Anthra-1'9'(*N*),10',(*N*),4'(or 5')-dipyridazones of the general formula I, where X and Y are H or univalent org. radicals,



(I)

are useful as optical bleaching agents for high polymers such as poly(ethylene terephthalate), poly(hexamethyleneadipamide), polycaprolactam, and cellulose acetate. The bleaching agents may be added to the polymer which is then melted and cast or spun, or the compds. may be mixed with the monomers prior to polymerization as in the case of poly(ethylene terephthalate). For example, 2 parts 2-butylanthra-1',9'(*N*)-pyridazone-5'-carboxylic acid (II) and 1 part $2,6\text{-Me}_2C_6H_3NHNH_2$ were heated at 220° for 30 min., cooled, stirred with 100 parts boiling 1% aq. NaOH, filtered, the ppt. stirred with 100 parts 1% HCl, and filtered to give pale yellow 2-(2,6-dimethylphenyl)-8-butylanthra-1',9'(*N*),10'-(*N*),5'-dipyridazone, m. 198–200° (EtOH). 1,5-Anthraquinonedicarboxylic acid (10 parts), 3 parts $BuNHNH_2$, and 1.3 parts NaOH were heated at 200° for 15 min., cooled, stirred with 200 parts boiling 1% aq. NaOH, filtered, 20 parts NaCl added to the filtrate, filtered, the ppt. dissolved in 300 parts $H_2O$, and acidified to ppt. II, m. 250°. Similarly prepd. were the following agents and intermediates (color and m.p. given): 2-(2,6-dimethylphenyl)anthra-1',9'(*N*)-pyridazone-5'-carboxylic acid, pale yellow, 310–12°; 2,8-diphenylanthra-1',9'(*N*),10'(*N*),5'-dipyridazone, greenish yellow, 391–3° [*o*-$Cl_2C_6H_4$ (III)]; 2,8-di-*p*-tolylanthra-1',9'(*N*),10'(*N*),5'-dipyridazone, —, <390°; 2,8-bis(2-chlorophenyl)anthra-1',9'(*N*),10'(*N*),5'-dipyridazone, pale yellow 400°; 2,8-bis(2,5-dichlorophenyl)anthra-1',9'(*N*),10'(*N*),5'-dipyridazone, pale yellow, 432°; 2,8-dibutylanthra-1',9'(*N*),10'(*N*),5'-dipyridazone, yellow, 185–6° (EtOH); 2,7-diphenylanthra-1',9'(*N*),10'(*N*),4'-dipyridazone, light greenish yellow, 394.5–6° (III); anthra-1',9'(*N*),10'-(*N*),5'-dipyridazone, light brown, >400°; 2,8-bis(2,6-dimethylphenyl)anthra-1',9'(*N*),10'(*N*),5'-dipyridazone, light yellow, 369° (III); 2,8-bis(2-hydroxyethyl)anthra-1',9'(*N*),-10'(*N*),5'-dipyridazone, yellow, 307° (III); 2-(2,6-dimethylphenyl)anthra-1',9'(*N*),10'(*N*),5'-dipyridazone, —, 348–50° (III); 2,8-bis(2,6-diethylphenyl)anthra-1',9'(*N*),10'-(*N*),5'-dipyridazone, pale yellow, 362°; 2-(2,6-diethylphenyl)anthra-1',9'(*N*),10'(*N*),5'-dipyridazone, —, 300°; 2,8-bis(*o*-bromophenyl)anthra-1',9'(*N*),10'(*N*),5'-dipyridazone, cream, —; 2-(6-chloro-2-methylphenyl)anthra-1',9'(*N*),10'(*N*),5'-dipyridazone, —, 349°; 2-(6-chloro-2-methylphenyl)anthra-1',9'(*N*)-pyridazone-5'-carboxylic acid, pale yellow, 305°; 2-(2,6-dichlorophenyl)anthra-1',9'(*N*),10'-(*N*),5'-dipyridazone, yellow, 379° (III); 2-(2,6-dichlorophenyl)anthra-1',9'(*N*)-pyridazone-5'-carboxylic acid, pale gray, 325°; anthra-1',9'(*N*)-pyridazone-5'-carboxylic acid, yellow, 389°; 2-(2,6-dimethylphenyl)-7-butylanthra-1',9'-(*N*)10'(*N*),4'-dipyridazone, pale yellow, 240–2°; 2-(2,6-dimethylphenyl)-anthra-1',9'(*N*)-pyridazone-4'-carboxylic acid, yellow, 283–7°; 2,7-dibutylanthra-1',9'(*N*).10'(*N*),4'-dipyridazone, pale yellow, 183° (III); 2,7-bis(*o*-chlorophenyl)anthra-1',9'(*N*),10'(*N*),4'-dipyridazone, pale cream, 412–14°; and 2,7-bis(2,6-dimethylphenyl)anthra-1',9'-(*N*),10'(*N*),4'-dipyridazone, pale yellow, 358°. I. L. Junk

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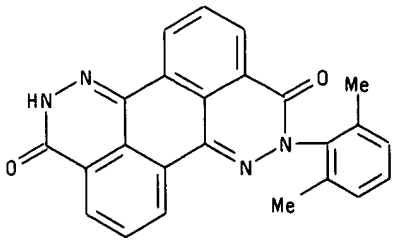
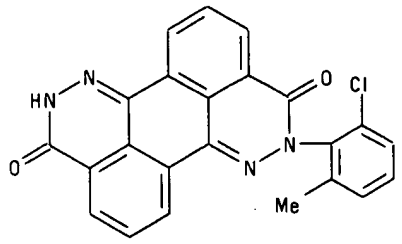
-57-

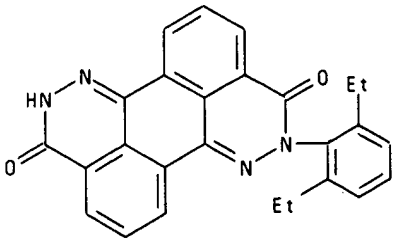
L14 ANSWER 30 OF 33 COPYRIGHT 1998 ACS
AN CA55:12868b CAOLD
DT Patent
IT ***114162-74-2*** ***114307-05-0*** ***122953-03-1***
RN 114162-74-2 CAOLD
CN Benzo[1,2,3-*de*:4,5,6-*d'e'*]diphthalazine-3,9-dione, 2,8-dihydro-2-(2,6-xylyl)- (6CI) (CA INDEX NAME)




RN 114307-05-0 CAOLD
CN Benzo[1,2,3-*de*:4,5,6-*d'e'*]diphthalazine-3,9-dione, 2-(6-chloro-*o*-tolyl)-2,8-dihydro- (6CI) (CA INDEX NAME)




RN 122953-03-1 CAOLD
CN Benzo[1,2,3-*de*:4,5,6-*d'e'*]diphthalazine-3,9-dione, 2-(2,6-diethylphenyl)-2,8-dihydro- (6CI) (CA INDEX NAME)

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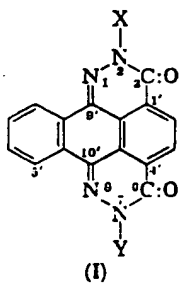

(I)

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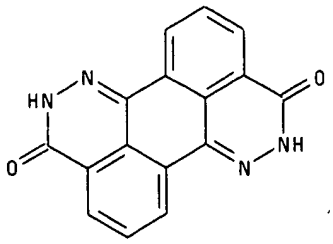
L14 ANSWER 31 OF 33 COPYRIGHT 1998 ACS
AN CA55:12868a CAOLD
DT Patent
IT ***34691-43-5***
RN 34691-43-5 CAOLD
CN Benzo[1,2,3-*de*:4,5,6-*d'e'*]diphthalazine-3,9-dione, 2,8-dihydro- (6CI, 9CI) (CA INDEX NAME)

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L14 ANSWER 32 OF 33 COPYRIGHT 1998 ACS
AN CA52:58460f CAOLD
DT Patent
IT ***120908-10-3***
RN 120908-10-3 CAOLD
CN 7*H*-Dibenzo[2,3:10,11]pyrrolo[2',3',4',5':6,7]piceno[12,13,14,1-*jklmnab*]phenanthridine-5,9,16(15*H*)-trione (6CI) (CA INDEX NAME)
*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

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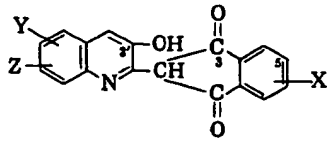
disperse dyes. I treated with tertiary bases gave quaternary ammonium compds., dyeing nitrogenous hydrophobic fibers in strong yellow shades of good fastness qualities, or condensed with $NH_3$ or primary or secondary amines gave compds., suitable as disperse dyes. 4-Amino-3'-hydroxy- *a* quinophthalone 42.4, $ZnCl_2$ 15, PhCl 330, iso-PrOH 32, and epichlorohydrin (II) 39 parts were refluxed with stirring for 1.5–2.0 hrs., cooled to 10°, petr. ether (III) (b. 30–60°) 400 added, the ppt. filtered off, washed with III 200, and dried at 50° ($ZnCl_2$ may be removed by exhaustive extn. with water) to give *4-(3-chloro-2-hydroxypropylamino)-3'-hydroxyquinophthalone* (IV), serving both as dye and intermediate. IV 8.0 in $(CH_2OH)_2$ 220 contg. $Me_3N$ 32 parts were heated slowly so that the temp. reached 95° in 1 hr. while passing *b* $Me_3N$ through the soln., the $Me_3N$-flow was then interrupted the soln. stirred for 1.5 hrs. at 95°, the cooled mass drowned in warm water 300 contg. sufficient HOAc to neutralize the soln., and filtered. The filtrate was treated with $ZnCl_2$ 5 and NaCl 60 parts, cooled to 0–5°, kept for 20 hrs., the product filtered off, and dried at 50° to give the *Zn complex* of the *trimethylammonium chloride* deriv. of IV. Similarly were prepd. the following quaternary compds. (intermediates given): IV and $Et_3N$; IV and $N(CH_2CH_2OH)_3$; IV and *c* $Et_2NCH_2CH_2OH$; IV and $PhCH_2NMe_2$; 5-amino-3'-hydroxyquinophthalone and II which gave the dye (V); V and $Me_3N$, isolated as the $ZnCl_2$ complex. Cf. *C.A.* 51, 14281*a*; following abstr. Raymond Blocher

Dyes of the quinophthalone series. Frithjof Zwilgmeyer (to E. I. du Pont de Nemours & Co.). U.S. 2,818,410, Dec. 31, 1957. Dyes of the general formula I were prepd., where X is a $O_2N$ or $H_2N$ group and Y and Z are H, Cl, Br,

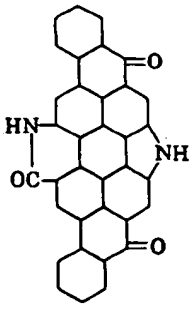


(I)

or a Me group. The I dye poly(ethylene terephthalate) *e* fiber, nylon, cellulose, acetate, and similar hydrophobic fibers in yellow shades of good fastness properties. 3-Nitrophthalic acid (II) 211, 2-methyl-3-hydroxy-4-quinolinecarboxylic acid 203, and *o*-$C_6H_4Cl_2$ (III) 2600 parts were heated for 18 hrs. at 165–70°, the mixt. cooled to room temp., agitated with 3% aq. NaOH 7000 and activated C 30, filtered, the III layer sepd., concd. HCl added to the aq. phase to pH 8, the ppt. filtered off, washed with water, and dried at 100° to give I (X = 4-$O_2N$, Y = Z = H)(IV). Similarly was prepd. the 5-$O_2N$ analog. EtOH 560, HOAc 525, and powd. Fe 170 parts were heated to 80°, the heat shut off, and IV 150 added at such a rate as to maintain the temp. at 80°. The mixt. was then stirred for 16 hrs. at 80°, drowned in NaOAc.$3H_2O$ 100 in water 5000 parts, stirred for 1 hr., the ppt. filtered off, washed with water, and dried at 100° to give the *4-amino-3'-hydroxyquinophthalone*. Similarly was prepd. the *5-$H_2N$ analog*. II treated as above with 2-methyl-3-hydroxy-6,8-dibromo-4-quinolinecarboxylic acid (V) gave I (X = 4-$O_2N$, Y = 6-Br, Z = 8-Br). Replace- *g* ment of V by 2-methyl-3-hydroxy-6-bromo-4-quinolinecarboxylic acid, 2-methyl-3-hydroxy-6,8-dichloro-4-quinolinecarboxylic acid, or 2,8-dimethyl-3-hydroxy-7-chloro-4-quinolinecarboxylic acid gave similar dyes. The corresponding *5-$O_2N$ isomers* were obtained when II was replaced by 4-nitrophthalic acid. Cf. preceding abstr. R. Blocher

Solution dyeing of cuprammonium rayon. Hin Yukawa, Masatoshi Sakamoto, and Mitsuo Koike (to Asahi Chemical Industry Co.). Japan. 6617('55), Sept. 17. The raw cellulosic material (I) used in the cuprammonium process is dyed by the dyes which can be insolubilized after absorption or formation on I, e.g., vat dyes, S dyes, or naphthol dyes. The dyed I or its mixture with undyed I is dissolved in the *h* cuprammonium soln. and spun in the ordinary manner. The dye in the spinning soln. and the fibers are very fine particles, hence the dispersion of dye is higher than in ordinary pigment and it is not dissolved out during spinning and finishing. Ryotaro Ito

Dyes of the dibenzanthrone series. Wilhelm Schmidt-Nickels (to General Aniline & Film Corp.). U.S. 2,819,270, Jan. 7, 1958. Black vat dyes of good stability are prepd. by heating $PhNO_2$, aminodibenzanthrone, and chloroethyl carbonate for 2 hrs. at 90–5°, for 2 hrs. at 130–5°, and for 2 hrs. at 170–5°. The solid reaction product 29.9 is filtered, heated at 155–60° with iodine 3 and $PhNO_2$ 450, Br 12.3 in $PhNO_2$ 60 parts is added; the mixt. is stirred for 4 hrs. at 155–60°. The filtered product of this second reaction 24 is then heated under pressure with aq. $NH_3$ 360 and cryst. $CuSO_4$ 3 parts to give a product I, which treated with Cl-$SO_2H$, pyridine, and Fe gives the leuco sulfuric ester salt of I.



(I)

E. Hirschhorn

Enhancing the acetate dyeability of vinylidene cyanide interpolymers. Geo. Gateff and Stephen M. Davis (to B. F. Goodrich Co.). U.S. 2,819,253, Jan. 7, 1958. Hydrolysis of vinylidene cyanide-interpolymer fibers before dyeing makes it possible to dye the fibers with acetate dyes to the same *d* depth as hydrophilic fibers. $HgSO_4$ is a particularly effective catalyst. Thus, to 20% solns. of a vinylidene cyanide:-vinyl acetate copolymer in (1) acetonitrile, (2) 95% dimethylformamide and 5% water, and (3) 94% acetone, 5% dimethylformamide, and 1% $H_2SO_4$, 1% $Hg(OAc)_2$ (based on wt. of polymer) was added and stirred for 15 min., followed by the amt. of $H_2SO_4$ required to react with the Hg salt. Thin films were cast from each soln. by pouring on hot plates at 50–60° and evapg. the solvent. Fibers were extruded from other portions of each soln. after stirring for 3 hrs. at 60–70°. All of the films were dyed in a satisfactory manner with a bath contg. 5% (based on film wt.) Eastman Blue BLT. Fibers formed from (1) did not dye well; those from (2) and (3) dyed satisfactorily, (3) being the best. Thomas A. Wilson

Waste gas-fast dyed cellulose derivatives. Carl Schuster, Karl Maier, Robert Gehm, Julius Eisele, and Wilhelm Frederkiel (to Badische Anilin- & Soda-Fabrik Akt.-Ges.). U.S. 2,813,774, Nov. 19, 1957. Small amts. of colorless *f* esters of hydroxyalkylamines added before, during, or after dyeing of cellulose derivs. prevent fading by atm. oxides of nitrogen. The esters are aromatic, araliphatic, cycloaliphatic, aliphatic, and carbamic acid esters. Thus, acetate rayon (I) 100 g. is dyed for 1 hr. at 75° in water 20 l., 1,4,5,-8-tetraaminoanthraquinone (II) 10 g., and *N,N'*-bis(2-benzoyloxyethyl)piperazine (III) 40 g. to give mid-blue, waste gas-fast shades. Similarly are used instead of III *N*-benzoyloxyethylimidazole, $BuN(CH_2CH_2O_2CPh)_2$, $MeN-(CH_2CH_2O_2CCH_2Ph)_2$, the bis(hexahydrobenzoate) of *N,N'*-bis(2-hydroxyethyl)piperazine (IV), the bis(phenylcarbamate) of $Me(HOCH_2CH_2)_2N$, the bis(phenylcarbamate) of IV, the tris(phenylcarbamate) of $(HOCH_2CH_2)_3N$, the phenylcarbamate of 2-dimethylamino-1-propanol (V), the phenylcarbamate of $Pr_2(HOCH_2CH_2)N$ (VI), the phenylcarbamate of *N*-vinyl-2-(hydroxymethyl)imidazole, the ester of 1 mole hexamethylene diisocyanate (VII) and 2 moles V, the ester of 1 mole of VII and 2 moles of VI, the bis(phenylcarbamate) of $Bu(HOCH_2CH_2)_2N$, the phenylcarbamate of *N*-(hydroxyethyl)pyrrolidine (VIII), the ester of 1 mole of methylphenylene diisocyanate and 2 moles VIII, the phenylcarbamate of 2-diethylamino-*N*-(hydroxyethyl)pyrrolidine, and the phenylcarbamate of $(Et_2NCH_2)_2CHOH$. Instead of II various other aminoanthraquinones are also used. Myrow N. Lugasch

Optical bleaching agents. René M. H. V. de Saint Aunay and Maurice L. Lefébvre (to Compagnie française des *i* matières colorantes). U.S. 2,813,864, Nov. 19, 1957. Optical bleaching agents of the general structure I have been prepd., in which A is an alkylene group, R is a COOH group or its salt, S and S' are H, $SO_3H$, or COOH groups, X is an H, alkyl, or hydroxyalkyl group, Y is an acylamino, substituted